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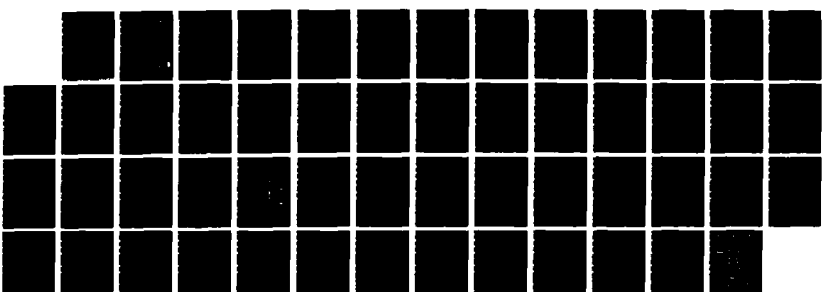

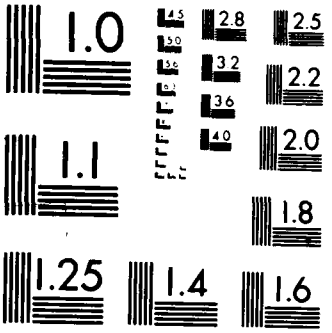
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Study of Energy Levels and Decay Mechanisms for Singlet Rydberg States of Molecular Nitrogen

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This report summarizes a series of investigations of the singlet Rydberg States of molecular nitrogen. The objective of the research was to use laser excitation out of a metastable singlet state in N_2 to study the energy levels and decay mechanisms for the high lying singlet Rydberg and valence states. The first section summarizes the current knowledge of these states. The second section describes the initial attempts to produce a beam of molecules in the $a''(0)^1\Sigma_g^+$ state and use laser excitation to gain access to higher lying singlet states. The third section describes the successful experiments in which laser excitation out of the $a''(0)^1\Sigma_g^+$ states was used to study the $c_4(0)^1\Pi_u$, $c_5'(0)^1\Sigma_u$, and $c_4'(3)^1\Sigma_u$ Rydberg states. The measured linewidths are used to determine the lifetimes of the $c_4(0)^1\Pi_u$ and $c_4'(3)^1\Sigma_u^+$ states.

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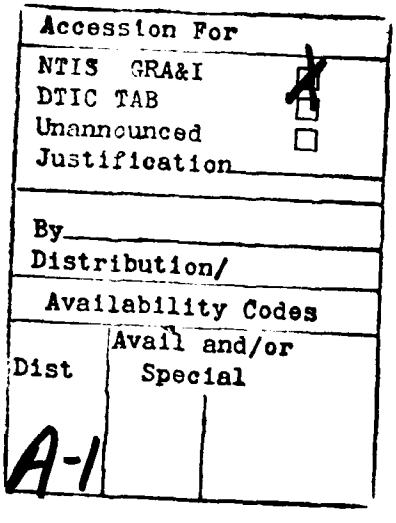

1.0 Introduction

The major aim of the work under this contract was to study the high lying Rydberg and valence states of N_2 and, if feasible, to ascertain whether or not they were sources of infrared radiation. It was proposed to use an electron beam to excite the N_2 molecules in a thermal beam to the $a''(0)^1\Sigma_g^+$ metastable state, one laser to excite the molecules to a higher state with a p character and a second laser to excite the molecules from the "p" state to a higher lying state with the character of an s or d orbital which could not decay optically to the ground state. At the time of this proposal, the lifetime of the $a''(0)^1\Sigma_g^+$ state was not known so it was uncertain whether or not the configuration of apparatus used earlier to measure the lifetimes of the vibrational levels of the $B^3\Pi_g$ state of N_2 could be used to study laser excitation out of the $a''(0)^1\Sigma_g^+$ metastable state. This report summarizes the research program which lead to the successful detection of laser excitation out of the $a''(0)^1\Sigma_g^+$ state and presents new data on the higher lying Rydberg states. The first part of this report summarizes the present knowledge of the singlet Rydberg levels; the second part describes the exploratory experiments through which it was learned how to observe laser excitation out of the $a''(0)^1\Sigma_g^+$ state; the third part summarizes the measurements on the high lying Rydberg states.

2.0 Studies of Higher Singlet States

2.1 Background Information

Despite their importance for understanding the behavior of excited N_2 molecules, little is known about the decay mechanisms for the high lying singlet states.[1] The failure to observe uv radiation in aurorae from the singlet states is still quite controversial.[2] The uv radiation from N_2 has been observed in Voyager I observations of emission from Titan's upper atmosphere.[3]

The term values for the singlet states that can be reached by optical absorption from the ground state have been studied extensively by Carroll, Yoshino, and their collaborators.[4-10] Gurtler, Saile, and Koch[11] used a synchrotron radiation source to study the photoabsorption cross section of N_2 in the range from 10-35 eV. The uv optical absorption is dominated by the $c_n{}^1\Pi_u$ and $c_n'{}^1\Sigma_u$ Rydberg states and the $b^1\Pi_u$ and $b'^1\Sigma_u$ valence states. The absorption spectra are quite complicated due to the interactions between the levels. The $c_n{}^1\Pi_u$ and $c_n'{}^1\Sigma_u$ states from a p complex[12] and there are homogeneous perturbations between the ($b^1\Pi_u$, $c_n{}^1\Pi_u$) and ($b'^1\Sigma_u$, $c_n'{}^1\Sigma_u$) pairs of levels. Dressler[13] played a major role in untangling the levels from the complex spectrum. Figure 1 shows potential curves for some of the important singlet states.

Several groups have studied the emission spectrum from N_2 in the range from 80 to 120 nm. The studies of the emission spectrum are difficult because of the large cross section for self absorption which distorts the spectrum and the many overlapping bands with varying intensity. The earlier observers were Birge and Hopfield,[14] Watson and Koontz,[15] Wilkinson and Houk,[16] and Tilford and Wilkinson.[17] More recently Zipf and McLaughlin[18] measured the emission spectrum for electron beam excited N_2. Zipf and Gorman[19] measured the electron excitation for the $b'^1\Sigma_u$ valence state. Morgan and Mentall[20] studied the emission spectrum for excitation by low energy electrons.

Recently, Roncin et al.[21] have employed a magnetically confined low pressure discharge to study with high resolution the uv light emitted in the range from 80 to 110 nm. They saw in emission many transitions not reported by earlier workers. The availability of the results from the high resolution absorption data made it possible for them to identify most of the lines. Figure 2 shows an energy level diagram for the known singlet states. Those states which have been observed in emission are marked with circles.

Several groups have used electron excitation and electron energy loss spectroscopy to measure the cross sections for excitation of the Rydberg states.[22] C. C. Lin and his coworkers have measured the cross section for electron excitation of the $c_4'(0)^1\Sigma_u$ Rydberg state[23] and have carried out calculations of the cross sections for excitation by electrons.[24] Stahel, Leon and Dressler[25] have taken the energy loss spectroscopy measurements of Geiger and Schroeder[26] as input and made extensive calculations to understand the complex dependence of the excitation cross sections on the character of the levels and the vibrational state. Figure 3 shows the energy loss spectrum observed by Geiger and Schroeder for 25 keV electrons with the scattering angle $\theta \leq 1 \times 10^{-4}$. Figure 4 shows a plot of the strengths for the transitions taken from the paper by Stahel, et al.[25]

Dressler and Hesser[27-28] have measured directly the radiative lifetimes for selected levels. Oertel, et al.[29] excited N_2 with synchrotron radiation and observed the fluorescence from some $^1\Pi_u$ and $^1\Sigma_u^+$ states. They made use of the pulsed character of the synchrotron radiation to measure the lifetimes for some of the levels.

Zipf and McLaughlin[18] used measurements of the cross section for production of light by electrons in conjunction with the excitation cross sections determined through energy loss spectroscopy[26] to estimate the relative branching ratios for radiative decay and predissociation. They concluded that many of the levels decay primarily through predissociation. Roncin, et al.[30] found evidence for predissociation of the $c_4'(6)^1\Sigma_u^+$ and $b'(20)^1\Sigma_u^+$ levels in the sharp breaking off of the rotational bands observed in high resolution ultraviolet emission spectra. There has been no report of direct evidence for predissociation in the lower Rydberg states or lower vibrational levels of the $b^1\Pi_u$ or $b'^1\Sigma_u$ valence states.

Early excitation curves showed that there was a level near 12.25 eV; the angular dependence and the voltage dependence of the excitation were that expected for a quadrupole transition.[31-34] This level was later observed by Ledbetter[35] in absorption studies of a shock tube generated plasma. The level was identified as the $^1\Sigma_g^+$ level predicted in the calculation of Mulliken[36] and has been designated the $a''(0)^1\Sigma_g^+$ level. This level is the singlet counterpart of the $E^3\Sigma_g^+$ state. Transitions from this state to the $c_4(0)^1\Pi_u$ and $c_5'(0)^1\Sigma_u^+$ Rydberg states were subsequently measured using optogalvanic spectroscopy in an rf discharge by Suzuki and Kakimoto.[37] Subsequently Miyazaki, Scheingraber, and Vidal[38] measured transitions to the $c_5'(0)^1\Pi_u$, $b'(16)^1\Sigma_u^+$, and $b'(17)^1\Sigma_u^+$ states using optogalvanic double resonance spectroscopy in a dc discharge.

2.2 Plan of Attack

Figure 4 shows an energy level diagram for the known singlet states of molecular nitrogen including the metastable $a''(0)^1\Sigma_g^+$ state. It was proposed to use an electron beam to excite the N_2 molecules in a thermal beam to the $a''(0)^1\Sigma_g^+$ state, to employ a dye laser to excite the molecules to the $c_4(0)^1\Pi_u$ and $c_5'(0)^1\Sigma_u^+$ Rydberg states, and to use the hard uv radiation emitted in the decay of the Rydberg states to detect the transitions. This method had been successfully used earlier to excite molecules to the $B^3\Pi_u$ state and measure the lifetimes for the vibrational levels of the $B^3\Pi_u$ state. The primary unknowns in the design of the experiment were the lifetime of the metastable $a''(0)^1\Sigma_g^+$ state and the branching ratio for radiative decay of the $c_4(0)^1\Pi_u$ and $c_5'(0)^1\Sigma_u^+$ Rydberg states. It was assumed that the lifetime of the $a''(0)^1\Sigma_g^+$ state was roughly the same as the measured 190 μsec lifetime for the $E^3\Sigma_g^+$ state[39,40] and that the branching ratios for radiative decay of the singlet Rydberg states was not zero. It was disturbing that there was no reported observation of the $a''(0)^1\Sigma_g^+$ state in molecular beam experiments[41] carried out to measure the

lifetimes of the metastable states of N_2. The measurements using shock tube excitation suggested that the lifetime of the $a''(0)^1\Sigma_g^+$ state could be as short as 10μsec.[35] It was known that the cross section for electron induced excitation of the $a''(0)^1\Sigma_g^+$ state was small.[42]

2.3 Exploratory Experiments

For the first attempt to detect the excitation of the $c_4(0)^1\Pi_u$ and $c_5'(0)^1\Sigma_g^+$ Rydberg states we used the same set up we employed for the measurement of the lifetimes for vibrational levels of the $B^3\Pi_g$ state.[43] The red sensitive photomultiplier tube was used to detect the fluorescent radiation. We first tried this experiment with a room temperature N_2 beam and observed what appeared to be small fluorescent signals. These signals disappeared when we cooled the beam. This suggested that the lifetime of the $a''(0)^1\Sigma_g^+$ state was short and that when the beam was cooled the atoms in this state did not live long enough to reach the region where the dye laser beam crossed the molecular beam. The background count rate in the photomultiplier was high due to radiation emitted by the excited N_2 atoms. This limited the sensitivity of the experiment.

For the second series of experiments we replaced the cooled photomultiplier tube by a channeltron detector which was sensitive to hard uv radiation, such as would be emitted by Rydberg states through direct decay to the ground state of N_2. In these experiments we observed some signals which were suggestive of fluorescent signals, but we were not able to increase the signal to noise ratio sufficiently to make them believable. The experiments were quite encouraging in that the background with the channeltron was low so that we were sensitive to smaller signals than with the red sensitive photomultiplier tube.

For the third series of experiments we reconfigured the apparatus so as to decrease as much as was mechanically feasible the distance from the source of

metastable molecules to the point where the laser beam intersected the molecular beam. We then used the channeltron detector to search for excitation of the $c_4(0)^1\Pi_u$ and $c_5'(0)^1\Sigma_u^+$ states. We were not able to detect any fluorescent radiation from the Rydberg states. The geometry of the apparatus was such that if the lifetime of the $a''(0)^1\Sigma_u$ state was less than 100μs, a sufficient number of metastable molecules to produce an observable signal would not reach the detector.

Since it was impossible to decrease further the distance between the metastable source and the laser interaction region without a major rebuilding of the apparatus, we started an investigation of other methods for obtaining a source of N_2 molecules in the $a''(0)^1\Sigma_g^+$ metastable state. It was particularly attractive to use a discharge source since we could easily decrease the distance between the discharge source and interaction region by bringing the beam in from the opposite end of the beam apparatus.

As a first step in this investigation we explored the use of optogalvanic spectroscopy as a means for determining the optimum discharge conditions for production of the $a''(0)^1\Sigma_g^+$ state. We were able to obtain very good optogalvanic signals in a cell. Figure 6 shows a chart recording of the $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ signals near the head of the Q band.

We then constructed a discharge tube with a hole in the end and installed it so that the end of the discharge was roughly 2cm from that laser interaction region. Figure 7 shows a diagram of the discharge tube source. It was estimated that it would require 30-40μs for discharge produced molecules in the $a''(0)^1\Sigma_g^+$ state to reach the laser interaction region. We saw good optogalvanic signals in the discharge although they were somewhat irreproducible and depended critically on the discharge conditions. We did not see any signals due to laser excitation out of the $a''(0)^1\Sigma_g^+$ state with this apparatus.

We then abandoned this approach and decided to construct a new apparatus in which the distance from the electron excitation to the laser interaction region could be minimized. We designed and constructed a new vacuum chamber which is much more flexible than the old one. We also built a new electron excitation source which had a larger magnetic field and for which the distance from the electron beam to the front of the source was less than 1 cm. With this new excitation source and the new chamber, the distance from the electron excitation to the laser interaction region was only 1 cm. For a thermal beam of N_2 this corresponds to 20μs. A mount for the channeltron detector was designed so that it viewed the laser interaction region with a spatial separation of 2 cm. We searched for but did not find signals with this arrangement. We observed, however, that when we cooled the source to liquid nitrogen temperature, the number of uv photons detected by the channeltron decreased as if there was a uv emitting component of the beam with a lifetime of approximately 2μs. We suspected that this might be due to light emitted by radiative decay of molecules in the $a''(0)^1\Sigma_g^+$ metastable state. This implied an average decay length for molecules in the $a''(0)^1\Sigma_g^+$ state of 1 mm.

We then decided to construct a configuration in which the electron beam excitation and the laser interaction took place in the same region such that the excited molecules would not have to travel between the electron excitation and the laser interaction. The uv sensitive channeltron was to be used to detect the transition. Figure 8 shows a schematic diagram of the initial arrangement. With this configuration we detected what we thought were signals but which could not be reproduced when we changed the arrangement in a manner which should have increased the signals. Two major problems with this arrangement were the high counting rate in the channeltron due to light from direct electron excitation of the high lying Rydberg states and the space charge limit to the intensity of the electron beam.

To test the sensitivity of this apparatus, we used a beam of neon. Neon has two near lying metastable states similar to the $a''(0)^1\Sigma_g^+$ state in nitrogen and through laser excitation out of these states, one can reach states which decay through the emission of hard uv radiation near 75 nm.[44] We were not able to observe signals in neon with this configuration of the apparatus.

We then decided to construct a diode detector with a tantalum foil photocathode and to use magnetic confinement to increase the intensity of the electron beam. The laser beam was chopped and a lock-in-detector was used to detect the signals. This arrangement is more sensitive than the earlier configuration because we could increase substantially the equivalent photon counting rate and see a much smaller fractional change in the uv light. With this set-up we were able to obtain very good signals which were quite reproducible.

2.4 Results

Figure 9 shows a schematic diagram of the apparatus successfully used to excite the N_2 molecules and to observe the transitions. A 30-35 eV, 4-5 mA magnetically collimated electron beam excites the N_2 molecules in a thermal beam. The collimation ratio for the N_2 beam is 10 to 1; the source pressure, 5 torr; the magnetic field in the source region, roughly 400G. The molecular beam and the electron beam are collinear and counterpropagate so as to maximize the region of overlap. The tantalum cathode photodiode monitors the uv light emitted perpendicular to the electron beam and is mounted immediately below the laser interaction region. The diode is estimated to have an average quantum efficiency[45] of approximately 10% over the region from 40 to 110nm. The electron beam excites the molecules to the $a''(0)^1\Sigma_g^+$ metastable state and a myriad of other short and long lived states, many of which decay with emission of uv light in the range from 40 to 110 nm. A laser beam perpendicular to the

electron beam and to the central axis of the photodetector excites the molecules in the metastable $a''(0)^1\Sigma_g^+$ state to higher Rydberg states. A light chopper modulates the laser beam and a lock-in detector measures the modulated component of the photocurrent. The absorption signals from an iodine cell are used to measure the wavelength of the laser.[46]

Figure 10 shows the signals observed for the Q branch $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g$ transitions together with the absorption signal from the iodine cell. The N_2 signals are due to an increase in the uv light detected; the change in the light intensity is roughly 6 parts in 10^5.

A similar experiment carried out to test the photodiode with the nitrogen replaced by neon gas gave signals with an increase in the uv light detected with low source pressures (0.4 torr) and a decrease with high source pressures. As the pressure increased the signal in the wings of the line changed sign first and then the signal at the center decreased and changed sign. This behavior was quite suprising. The $1s_5(^3P_2)$ metastable level in neon, which corresponds to the $a''(0)^1\Sigma_g^+$ state, does not decay with emission of uv radiation; the $1s_2(^1P_1)$ and $1s_4(^3P_1)$ levels, which are populated through radiative decay after laser excitation to the $2p_2(^3P_1)$ level, decay rapidly with the emission of uv radiation.[44] Thus one would expect to see an increase in the uv light emitted. The change in the sign of the signal is attributed to a combination of reabsorption of the emitted uv radiation and laser depopulation of the metastable atoms which play a role in the electron excitation to higher levels which emit uv radiation. The nitrogen is less susceptible to this reversal since the emitted uv light comes in large part from transitions to higher vibrational levels of the ground state which are not populated at room temperature and the $a''(0)^1\Sigma_g^+$ state has a shorter lifetime than the metastable states in neon.

The only observation of uv light emitted by the $a''(0)^1\Sigma_g^+$ state is that reported by Lutz.[47] Dressler and Lutz[34] used the absorption in nitrogen gas at several pressures to observe the absorption band for the transition $a''(0)^1\Sigma_g^+ \leftarrow X(0)^1\Sigma_g^+$. Lutz subsequently reported the observation of the $a''(0)\Sigma_g^+ \rightarrow X(0)^1\Sigma_g$ transition in emission from a discharge at 101.005 nm. The near lying intense bands from the other transitions make the observation of this transition difficult. Lutz's observation of emission has not been confirmed by later workers. The term value 99005.0 cm^{-1} calculated from the wavelength measured by Lutz differs by 165 cm^{-1} from the term value 98840.55 cm^{-1} derived in a recent analysis by Yoshino and Freeman.[9] It is assumed that the shift is due to collisions with other N_2 molecules in the gas and that the absorption is due to an induced dipole transition.

This same technique has been used to observe transitions from the $a''(0)^1\Sigma_g^+$ state to the $c_5'(0)^1\Sigma_u^+$ and the $c_4'(3)^1\Sigma_u^+$ states. In each case the signals were due to an increase in the uv light detected and the linewidths were comparable to that for the $c_4(0)^1\Pi_u$ state.

The change in the uv light emitted was roughly the same for all three transitions. If the change in the light emitted is due simply to the emission by the laser excited $c_4(0)^1\Pi_u$, $c_5'(0)^1\Sigma_u^+$ and $c_4'(3)^1\Sigma_u^+$ states, then this does not support the conclusion of Zipf and McLaughlin[18] concerning predissociation in the excited singlet states of N_2. Zipf and McLaughlin concluded that the $c_4'(3)^1\Sigma_u^+$ state decayed through predissocation 15% of the time and the $c_4(0)^1\Pi_u$ and $c_5'(0)^1\Sigma_u^+$ states decayed through predissociation more than 99% of the time. Roncin *et al.*[21] reported that the uv radiation from the $c_4'(3)^1\Sigma_u^+$ state is very strong, the uv radiation from the $c_4(0)^1\Pi_u$ state is weak, and uv radiation from the $c_5'(0)^1\Sigma_u^+$ state is very weak. There are clearly discrepancies between these observations which merit further investigation.

Figure 11a shows the observed profile for the Q(12), $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ transition. A fit to a Voigt line profile gives (350±80) MHz for the Lorentzian component and (630±70) MHz for the Gaussian component. The width of the Lorentzian component corresponds to a lifetime of (0.46±0.10) nsec. Figure 11(b) shows a line profile for the $c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transition. For this transition the widths of the Lorentzian and Gaussian components are (640±130) MHz and (530±100) MHz respectively. The width of the Lorentzian component corresponds to a lifetime of (0.25±0.05) nsec. These two lifetimes are similar to the other reported lifetimes for singlet states of N_2. Table 1 summarizes the lifetimes reported for both the singlet Rydberg states and the $b^1\Pi_u$ and $b'^1\Sigma_u^+$ valence states.[27-29]

Table 2 summarizes the measured line positions for each of the transitions observed. Also shown are the line positions determined by Suzuki and Kakimoto[37] for the same transitions through optogalvanic spectroscopy or calculated from the uv absorption measurements of Yoshino, Freeman, and Tanaka.[8] In all cases the agreement is excellent.

In addition to these transitions, we searched for, but did not find, a number of other transitions. Table 3 summarizes all the transitions for which a search was made. It is not clear why we were not able to see transitions to the $b'^1\Sigma_u^+$ valence states.

We also searched for excitation to a higher lying Rydberg state with an electron in a d orbital. One laser was used to drive the $c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transition and a second laser was swept over the range expected for a $(nd)^1\Pi_g \leftarrow c_4'(3)^1\Sigma_u^+$ transition. The emitted uv light was monitored to look for a signal. We did not detect any transitions. This is not surprising since this method of observing a second transition is limited in sensitivity by the stability of the first laser. A better method would be to use an ion detector

to look for N_2^+ molecules produced through autoionization of the nd states. We plan in the future to use this method to look for such transitions.

2.5 Conclusions

A combination of electron beam and laser excitation has been used to observe the $c_4(0)^1\Pi_u$, $c_5'(0)^1\Sigma_u$, and $c_4'(3)^1\Sigma_u$ Rydberg states of N_2. The data indicate that all three of these states decay with roughly equal probability by emission of uv light. The measured lifetimes of the $c_4(0)^1\Pi_u$ and $c_4'(3^1\Sigma_u$ states are (0.46±0.10) and (0.25±0.05) nsec, respectively.

This technique provides a new and powerful method for studying the high lying singlet states in N_2. The addition of a uv spectrometer to observe the redistribution of the radiation would make it possible to observe transitions to other Rydberg states, to observe transitions to the $b^1\Pi_u$ and $b'^1\Sigma_u$ valence states, to study the levels in greater detail, to measure the relative branching ratios for radiative decay and predissociation, to measure for each state the branching ratios for decay to the different vibrational levels of the ground state, and to measure the branching ratios for decay to the $a^1\Pi_g$ metastable state. Two lasers can be used to extend the measurements to the s and d Rydberg levels which are not accessible by optical absorption from the ground state.

3.0 References

1. For a comprehensive review of the data on the nitrogen molecule available prior to 1977, see A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
2. T. G. Slanger, Planet. Space Sci. 31, 1525 (1983).
3. D. F. Strobel and D. E. Shemansky, J. Geophysic. Res. 87, 1361 (1982).
4. P. K. Carroll, C. P. Collins, and K. Yoshino, J. Phys. B3, L127 (1970).
5. P. K. Carroll and K. Yoshino, J. Phys. B5, 1614 (1972).
6. K. Yoshino, Y. Tanaka, P. K. Carroll, and P. Mitchell, J. Mol. Spectrosc. 54, 87 (1975).
7. K. Yoshino, and Y. Tanaka, J. Mol. Spectrosc. 66, 219 (1977).
8. K. Yoshino, D. E. Freeman, and Y. Tanaka, J. Mol. Spectrosc. 76, 153 (1979).
9. P. K. Carroll and C. P. Collins, Can. J. Phys. 47, 564 (1969).
10. K. Yoshino and D. E. Freeman, Can. J. Phys. 62, 1478 (1984).
11. P. Gurtler, V. Saile, and E. E. Koch, Chem. Phys. Lett. 48, 245 (1977).
12. P. K. Carroll, J. Chem. Phys. 58, 3597 (1973).
13. K. Dressler, Can. J. Phys. 47, 347 (1969).
14. R. T. Birge and J. J. Hopfield, Astrophys. J 68, 257 (1928).
15. W. W. Watson and P. G. Koontz, Phys. Rev. 46, 32 (1934).
16. P. G. Wilkinson and N. B. Houk, J. Chem. Phys. 24, 528 (1956).
17. S. G. Tilford and P. G. Wilkinson, J. Mol. Spectrosc. 12, 231 (1964).
18. E. C. Zipf and R. W. McLaughlin, Planet. Space Sci. 26, 449 (1978).
19. E. C. Zipf and M. R. Gorman, J. Chem. Phys. 73, 813 (1980).
20. M. D. Morgan and J. E. Mentall, J. Chem. Phys. 78, 1747 (1983).
21. J.-Y. Roncin. F. Launey, and K. Yoshino, Planet. Space Sci. 35, 267 (1987).

22. E. N. Lassettre in Methods of Experimental Physics, Ed. by D. Williams (Academic Press, New York, 1974) Vol. 3, Part B, P. 868.

23. A. R. Filipelli, S. Chung, and C. C. Lin, Phys. Rev. A29, 1709 (1984).

24. S. Chung and C. C. Lin, Phys. Rev. A6, 988 (1972).

25. D. Stahel, M. Leoni, and K. Dressler, J. Chem. Phys. 79, 2541 (1983).

26. J. Geiger and B. Schroeder, J. Chem. Phys. 50, 7 (1969).

27. J. E. Hesser and K. Dressler, J. Chem. Phys. 45, 3149 (1966).

28. J. E. Hesser, J. Chem. Phys. 48, 2518 (1968).

29. H. Oertel, M. Kratzat, J. Imschweiler, and T. Noll, Chem. Phys. Lett. 82, 552 (1981).

30. J.-Y. Roncin, F. Launay, and Larzilliere, Phys. Rev. Lett. 53, 159 (1984).

31. H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, J. Chem. Phys. 44, 355 (1966).

32. E. N. Lassettre, A. Skerbele, and V. D. Meyer, J. Chem. Phys. 45, 3214 (1966).

33. A. Kupperman, J. K. Rice and S. Trajmar, J. Phys. Chem. 72, 3894 (1966).

34. K. Dressler and B. L. Lutz, Phys. Rev. Lett. 19, 1219 (1967).

35. J. W. Ledbetter, Jr., J. Mol. Spectrosc. 42, 100 (1972).

36. R. S. Mulliken, in The Threshold of Space (M. Zelikoff, Ed.) (Pergamon Press, New York, 1957) p. 169.

37. T. Suzuki and M. Kakimoto, J. Mol. Spectrosc. 93, 423 (1982).

38. K. Miyazaki, H. Scheingraber, and C. R. Vidal, Phys. Rev. Lett. 50, 1046 (1983).

39. W. L. Borst and E. C. Zipf, Phys. Rev. A3, 979 (1971).

40. R. S. Freund, J. Chem. Phys. 50, 3734 (1969).

41. R. S. Freund, J. Chem. Phys. 51, 1979 (1969).

42. D. C. Cartwright, S. Trajmar, A. Chutjian, and W. Williams, Phys. Rev. A16, 1041 (1977)

43. E. E. Eyler and F. M. Pipkin, J. Chem. Phys. 79, 3654 (1983).

44. N. B. Bhaskar and A. Lurio, Phys. Rev. A13, 1484 (1976).

45. J. A. R. Samson, in Techniques of Vacuum Ultraviolet Spectroscopy (John Wiley and Sons, New York, 1967), p. 229.

46. S. Gerstenkorn and P. Luc, Atlas du Spectre D'Absorption de la Molecule D'Iode (CRNS, Paris, 1978). A systematic correction is described by S. Gerstenkorn and P. Luc, Rev. Phys. Appl. 14, 791 (1979).

47. B. L. Lutz, J. Chem. Phys. 51, 706 (1969).

4.0 Tables

4.1 Table 1. Reported lifetimes for $^1\Pi_u$ and $^1\Sigma_u^+$ states of molecular nitrogen.

Electronic State		Lifetime (ns)		
		Oerzel, et al.[28]	Hesser and Dressler[26]	This Work
$b^1\Pi_u$,	v'=0	0.27±0.04		
$b^1\Pi_u$,	v'=1	1.75±0.26		
$b'^1\Sigma_u^+$,	v'=1	1.13±0.17		
$b'^1\Sigma_u^+$,	v'=5	0.28±0.04		
$b'^1\Sigma_u^+$,	v'=7	0.93±0.14		
$b'^1\Sigma_u^+$,	v'=9	0.71±0.11		
$b'^1\Sigma_u^+$,	v'=11	0.25±0.04		
$b'^1\Sigma_u^+$,	v'=12	0.25±0.04		
$c_4'^1\Sigma_u^+$,	v'=0		0.9±0.2	
$c_4'^1\Sigma_u^+$,	v'=2	0.65±0.10		
$c_4'^1\Sigma_u^+$,	v'=3			0.25±0.05
$c_4{}^1\Pi_u^+$,	v =0			0.46±0.10
$o_3{}^1\Pi_u$,	v'=2	0.30±0.05		

4.2 Table 2. A summary of the observed transition intervals in cm^{-1}. The other measurements for the $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ and $c_5^f(0)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g$ transitions are those of Suzuki and Kakimoto.[37] The intervals for the $c_4'(3)^1\Sigma_u \leftarrow a''(0)^1\Sigma_g$ transitions were calculated from the term values determined by Yoshino, et al.[8]

Transition	Other Work	This Work	Difference
	$c_4'(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$		
Q(1)	16725.154	16725.150±0.010	-0.004
Q(2)	16720.202	16725.197±0.004	-0.005
Q(3)	16725.271	16725.266±0.003	-0.005
Q(4)	16725.363	16725.359±0.003	-0.003
Q(5)	16725.476	16725.470±0.003	-0.006
Q(6)	16725.608	16725.599±0.005	-0.009
Q(7)	16725.765	16725.758±0.011	-0.007
Q(8)	16725.883	16725.888±0.019	+0.005
Q(12)	16727.037	16727.022±0.010	-0.015
R(1)	16732.769	16732.759±0.010	-0.009
R(6)	16751.416	16751.398±0.010	-0.018
R(14)	16776.607	16776.592±0.010	-0.015
	$c_5'(0)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$		
P(14)	16845.886	16845.877±0.010	-0.009
	$c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$		
R(6)	11825.133±0.300	11825.172±0.010	0.039
R(7)	11823.494±0.300	11823.695±0.010	0.201
R(8)	11821.308±0.300	11821.399±0.005	0.091

4.3 Table 3. Summary of transitions out of the $a''(0)^1\Sigma_g$ state of N_2 searched for and observed.

1.	$c_4(0)^1\Pi \leftarrow a''(0)^1\Sigma_g^+$	
	P branch: J=4	observed
	Q branch: J=1-8, 12-14	observed
	R branch: J=1,6,14	observed
2.	$c_4'(0)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$	
	P branch: J=14	observed
	R branch: J=6	observed
	R branch: J-1-3,13	NOT observed
3.	$c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$	
	R branch: J=6-8	observed
4.	$c_3(3)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$	
	Q branch: J=8	NOT observed
5.	$b(4)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$	
	Q branch: J=8	NOT observed
6.	$b'(10)^1\Sigma_g^+ \leftarrow a''(0)^1\Sigma_g^+$	
	R branch: J=8	NOT observed
7.	$b'(17)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$	
	R branch: J=2,4,6,10,14	NOT observed
8.	$b'(19)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$	
	R branch: J=22	NOT observed

5.0 Figures

5.1 Figure Captions

Fig. 1 -- The potential energy curves for the states of the nitrogen molecule relevant to the measurements summarized in this report.

Fig. 2 -- An energy level diagram showing the singlet levels of the N_2 molecule. Those levels which have been observed in emission are marked with a small circle.

Fig. 3 -- The energy loss spectrum for 25 keV electrons with a scattering angle $\theta \leq 1 \times 10^{-4}$. From Geiger and Schroeder (ref. 26).

Fig. 4 -- The calculated perturbed and deperturbed intensities for N_2 $^1\Pi_u \leftarrow X^1\Sigma_g^+$ (v=0) transitions. The valence $b^1\Pi_u$, Rydberg $c^1\Pi_u$ ($3p\pi$), and Rydberg $o^1\Pi_u$ (N_2^+ $A^2\Pi_u$, $3s\sigma$) states interact strongly, giving rise to the strong variations in the spectrum. The dotted lines show the Franck-Condon envelopes for the deperturbed states. The solid lines are the calculated intensities for transitions into strongly mixed eigenstates. After Stahel, et al., Ref. 25.

Fig. 5 -- Energy level diagram showing the excitation scheme used to observe the Rydberg states.

Fig. 6 -- The optogalvanic signal obtained with a DC discharge. The peak at the center is the band head for the Q band of the transition $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$.

Fig. 7 -- Discharge source used to produce metastable N_2 molecules.

Fig. 8 -- The first version of the apparatus in which the electron beam excitation and the laser interaction took place in the same region of space.

Fig. 9 -- The final configuration used to excite and observe the Rydberg states of N_2.

Fig. 10 - The signals for the Q branch of the $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ transitions near the band head.

Fig. 11 - The observed line profiles and the fits to a Voigt line profile for the Q(12), $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ and R(8), $c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transitions.

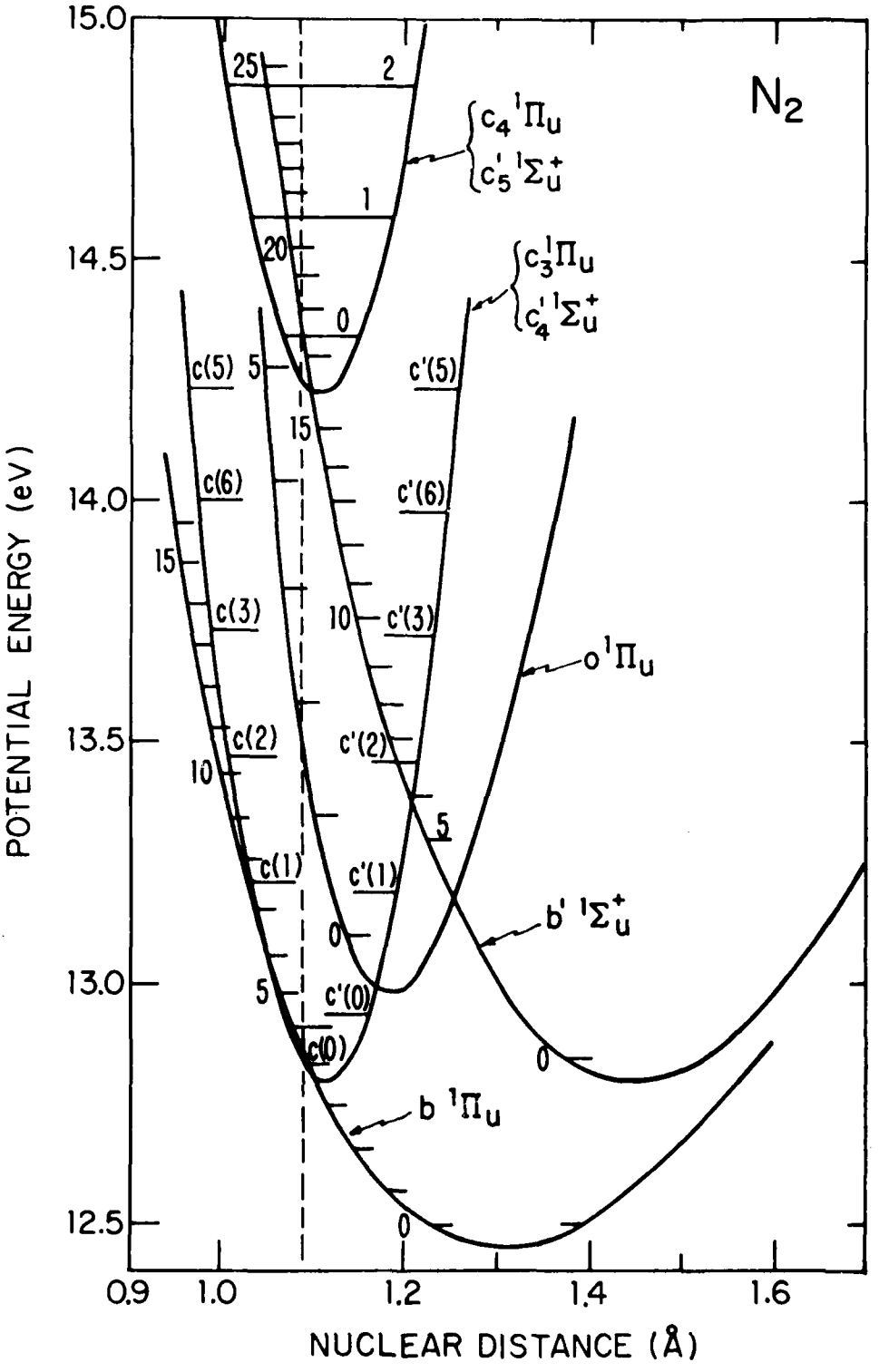
15.0
14.5
14.0
13.5
13.0
12.5
0.9
1.0
1.2
1.4
1.6
POTENTIAL ENERGY (eV)
NUCLEAR DISTANCE (Å)
N2
c4 1Πu
c'5 1Σ+u
c3 1Πu
c'4 1Σ+u
o 1Πu
b' 1Σ+u
b 1Πu
c(5)
c(6)
c(3)
c(2)
c(1)
c(0)
c'(5)
c'(6)
c'(3)
c'(2)
c'(1)
c'(0)
25
2
1
20
0
5
15
10
15
10
5
0
5
0
0

Figure 1

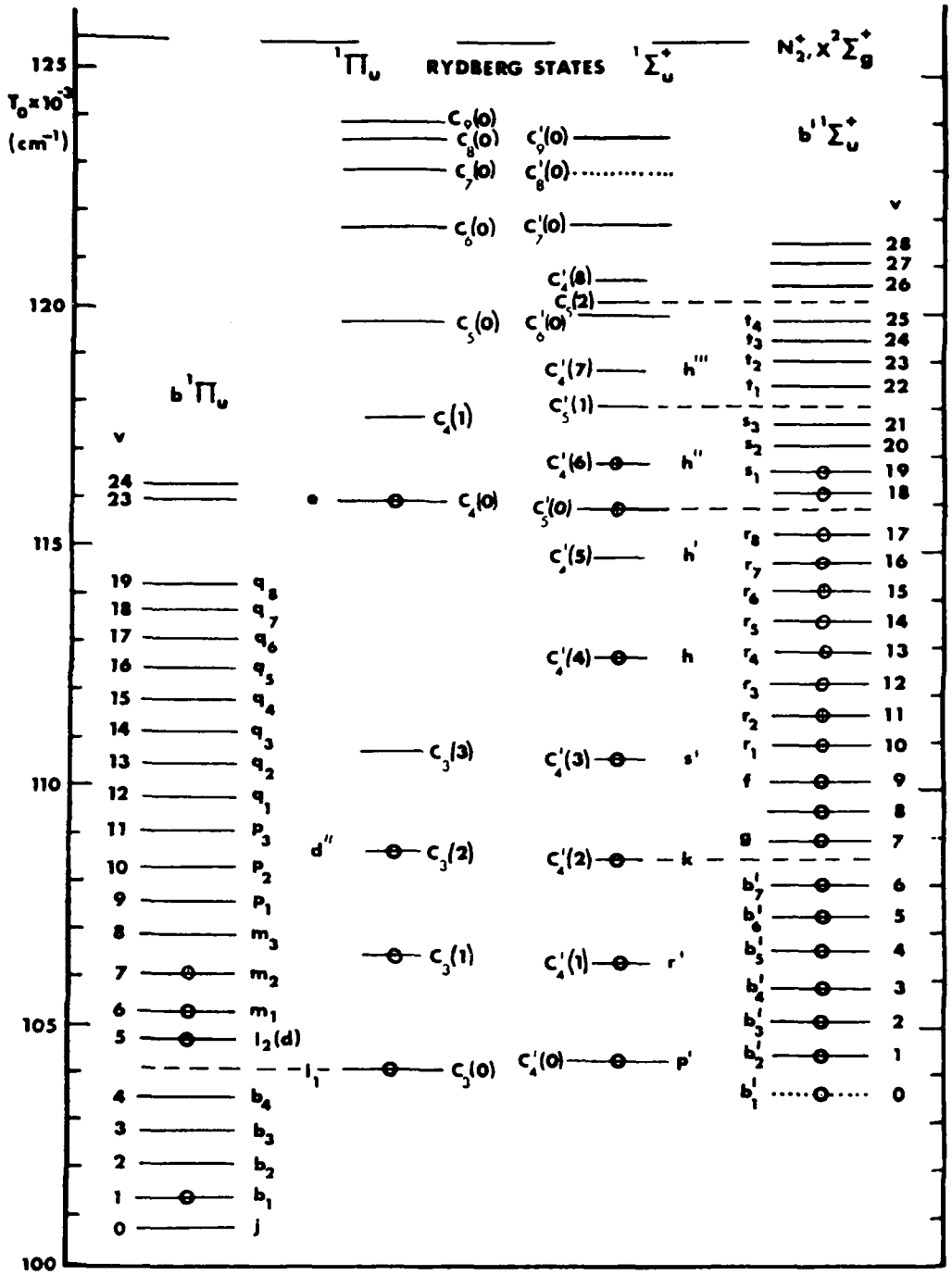
RYDBERG STATES
$^1\Pi_u$
$^1\Sigma_u^+$
$N_2^+, X^2\Sigma_g^+$
$b'^1\Sigma_u^+$
$b^1\Pi_u$
$T_0 \times 10^{-3}$ (cm^{-1})
125
120
115
110
105
100
v
$c_9(0)$
$c_8(0)$
$c_7(0)$
$c_6(0)$
$c_5(0)$
$c_4(1)$
$c_4(0)$
$c_3(3)$
$c_3(2)$
$c_3(1)$
$c_3(0)$
$c_9'(0)$
$c_8'(0)$
$c_7'(0)$
$c_4'(8)$
$c_5'(2)$
$c_6'(0)$
$c_4'(7)$
$c_5'(1)$
$c_4'(6)$
$c_5'(0)$
$c_4'(5)$
$c_4'(4)$
$c_4'(3)$
$c_4'(2)$
$c_4'(1)$
$c_4'(0)$
h'''
h''
h'
h
s'
k
r'
p'
d''
q_8 q_7 q_6 q_5 q_4 q_3 q_2 q_1
p_3 p_2 p_1
m_3 m_2 m_1
$l_2(d)$ l_1
b_4 b_3 b_2 b_1 j
t_4 t_3 t_2 t_1
s_3 s_2 s_1
r_8 r_7 r_6 r_5 r_4 r_3 r_2 r_1
f
g
b_7' b_6' b_5' b_4' b_3' b_2' b_1'
28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

Figure 2

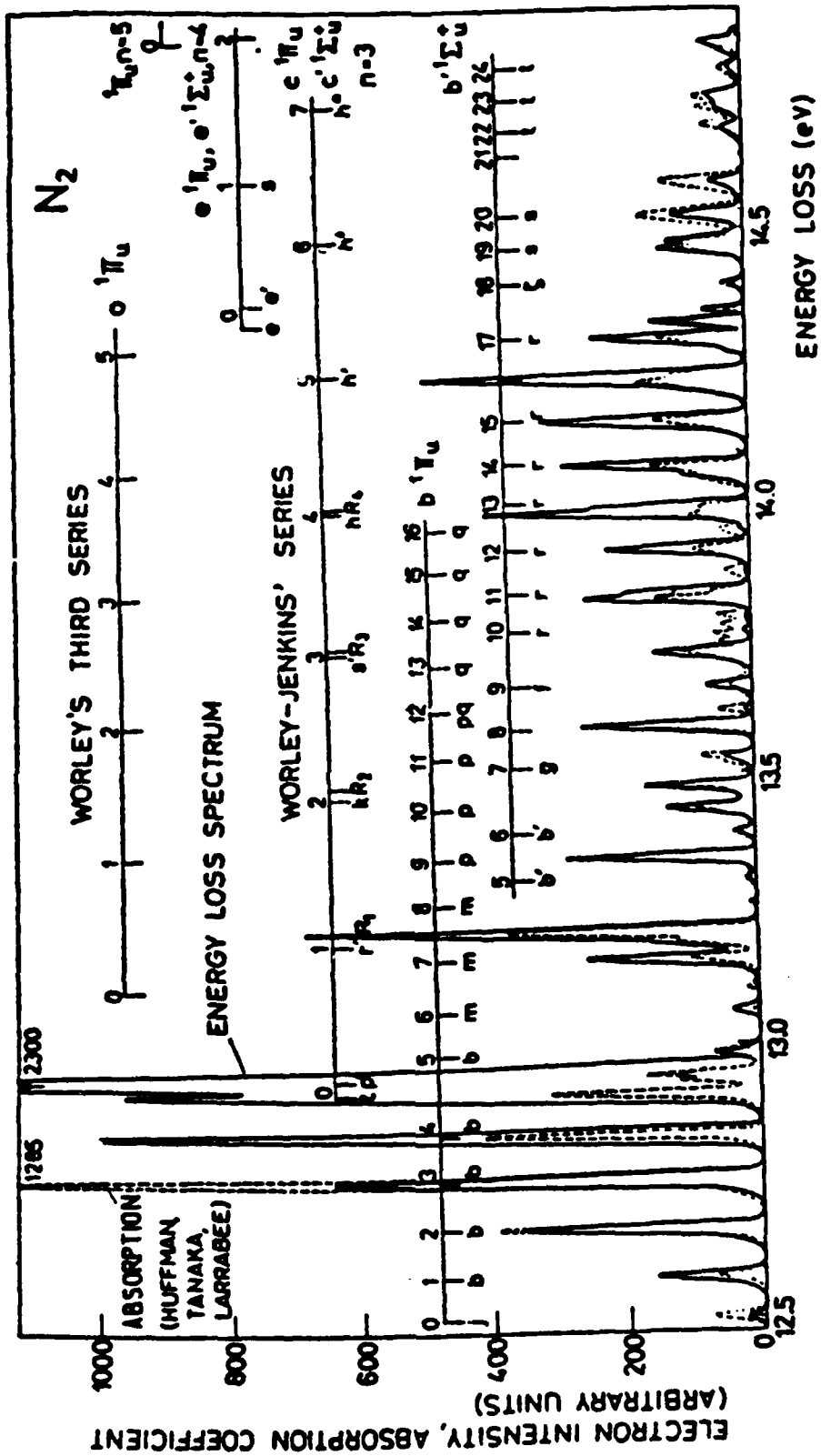
N_2
WORLEY'S THIRD SERIES
ENERGY LOSS SPECTRUM
WORLEY-JENKINS' SERIES
ABSORPTION (HUFFMAN, TANAKA, LARRABEE)
ENERGY LOSS (eV)
ELECTRON INTENSITY, ABSORPTION COEFFICIENT (ARBITRARY UNITS)

Figure 3

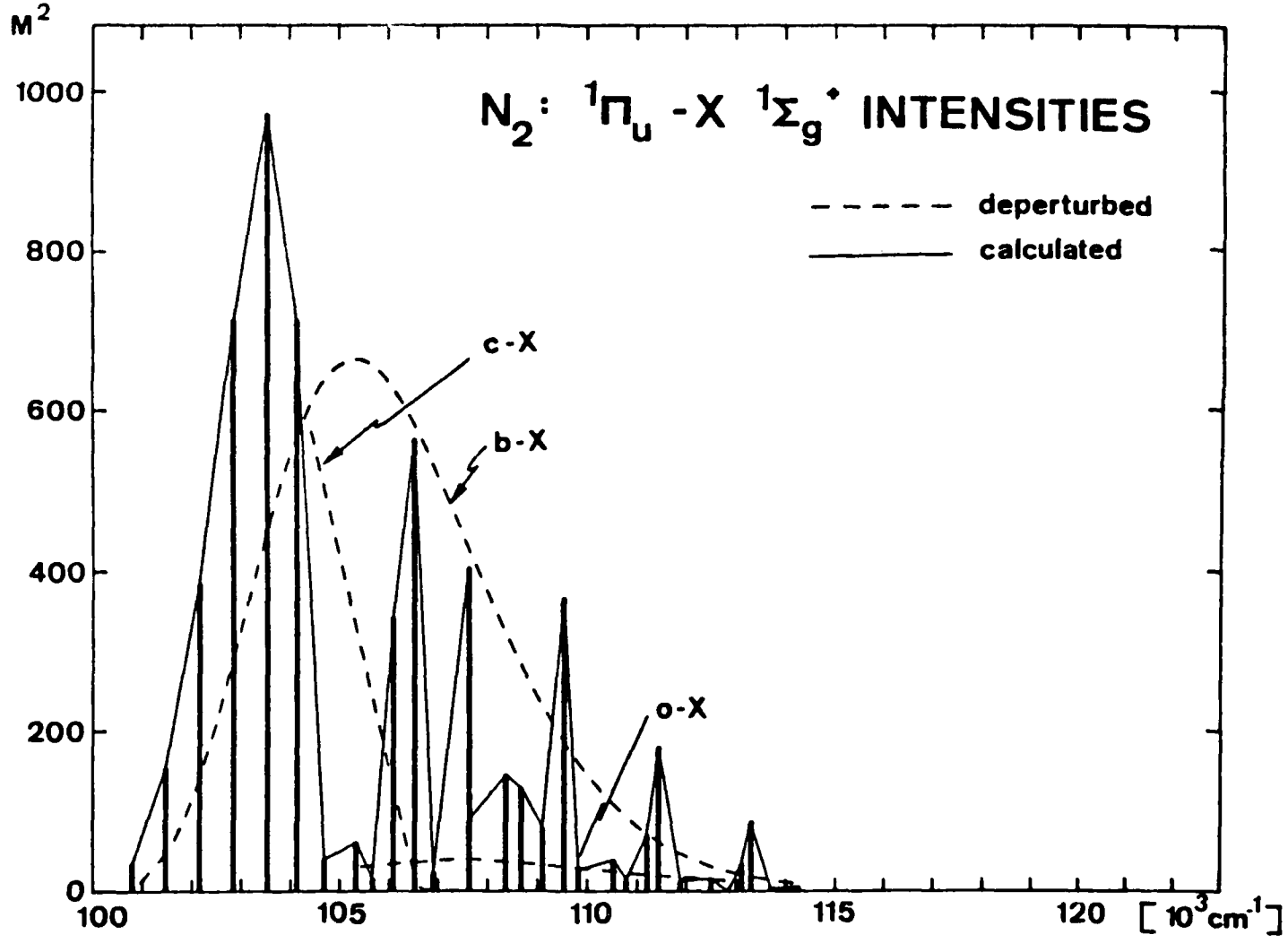
M²
1000
800
600
400
200
0
N₂: ¹Πu -X ¹Σg⁺ INTENSITIES
deperturbed
calculated
c-X
b-X
o-X
100
105
110
115
120
[10³cm⁻¹]

Figure 4

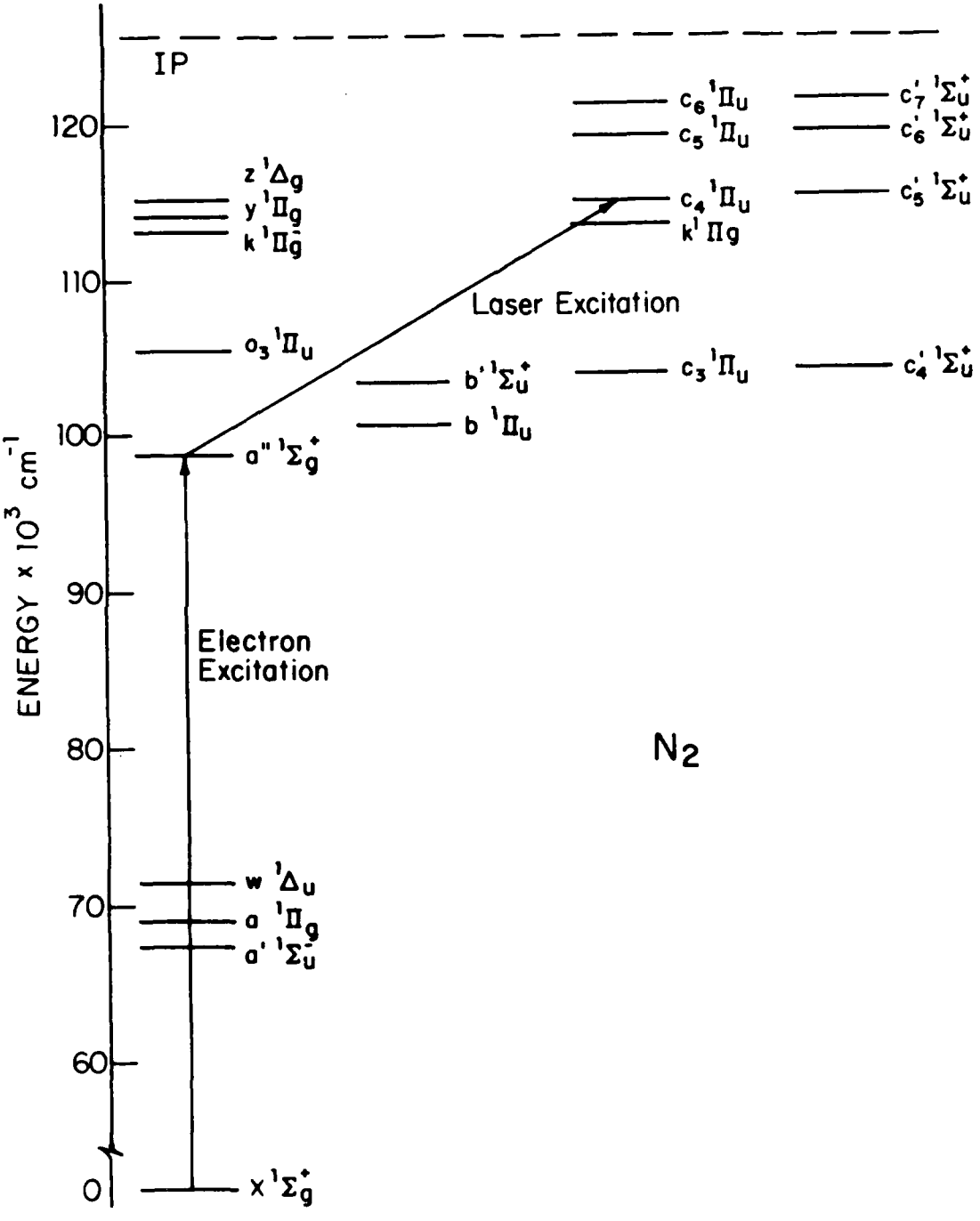
IP
120
110
100
90
80
70
60
0
ENERGY x 10^3 cm^{-1}
$z\,^1\Delta_g$
$y\,^1\Pi_g$
$k\,^1\Pi_g$
$o_3\,^1\Pi_u$
$a''\,^1\Sigma_g^+$
$w\,^1\Delta_u$
$a\,^1\Pi_g$
$a'\,^1\Sigma_u^-$
$x\,^1\Sigma_g^+$
Electron Excitation
Laser Excitation
$b'\,^1\Sigma_u^+$
$b\,^1\Pi_u$
$c_6\,^1\Pi_u$
$c_5\,^1\Pi_u$
$c_4\,^1\Pi_u$
$k'\,^1\Pi_g$
$c_3\,^1\Pi_u$
$c_7'\,^1\Sigma_u^+$
$c_6'\,^1\Sigma_u^+$
$c_5'\,^1\Sigma_u^+$
$c_4'\,^1\Sigma_u^+$
N_2

Figure 5

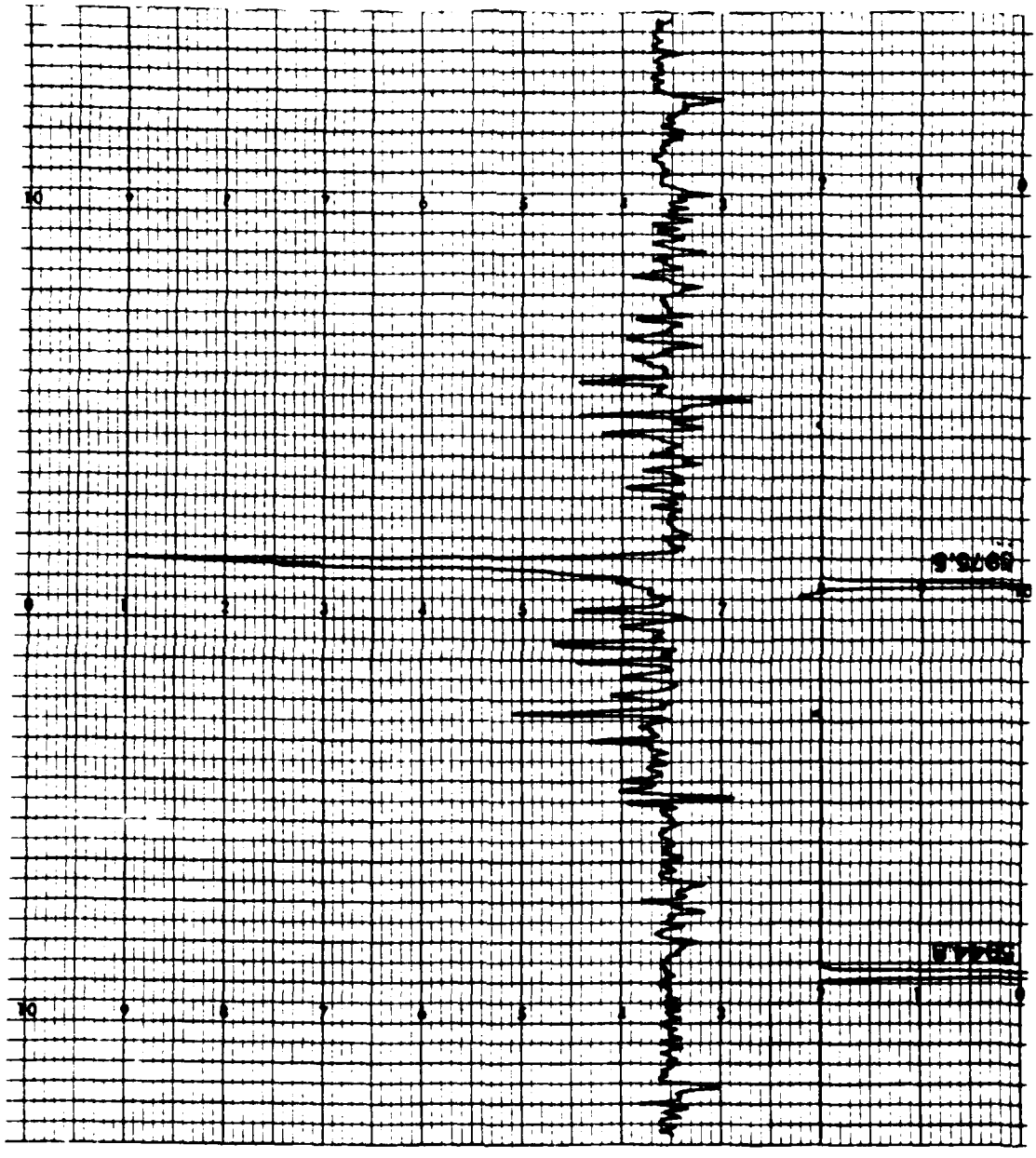

Figure 6

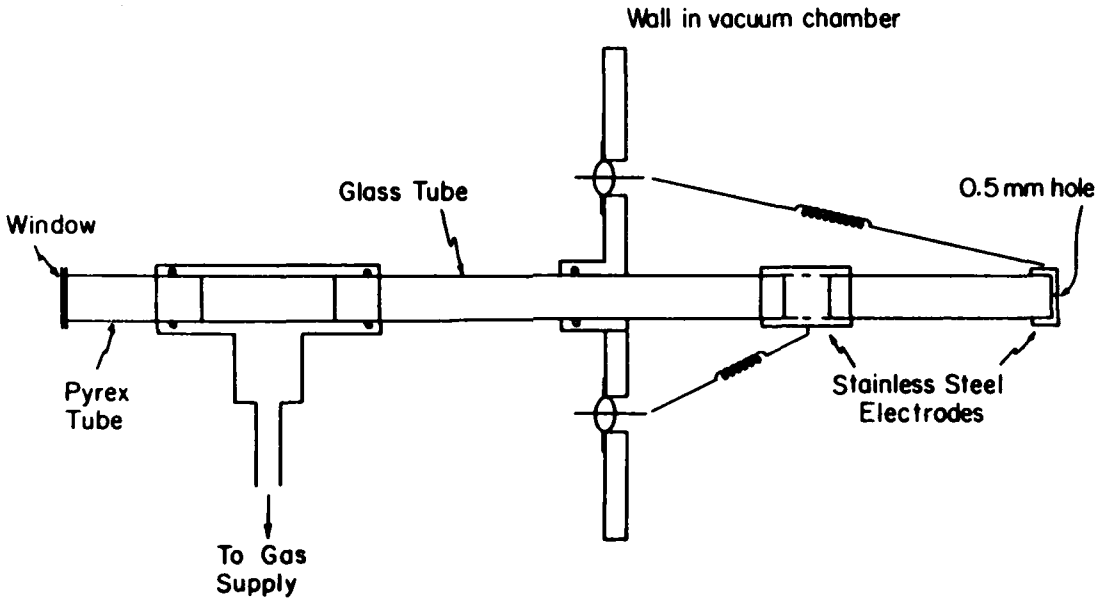
Wall in vacuum chamber
Glass Tube
0.5 mm hole
Window
Pyrex
Tube
Stainless Steel
Electrodes
To Gas
Supply

Figure 7

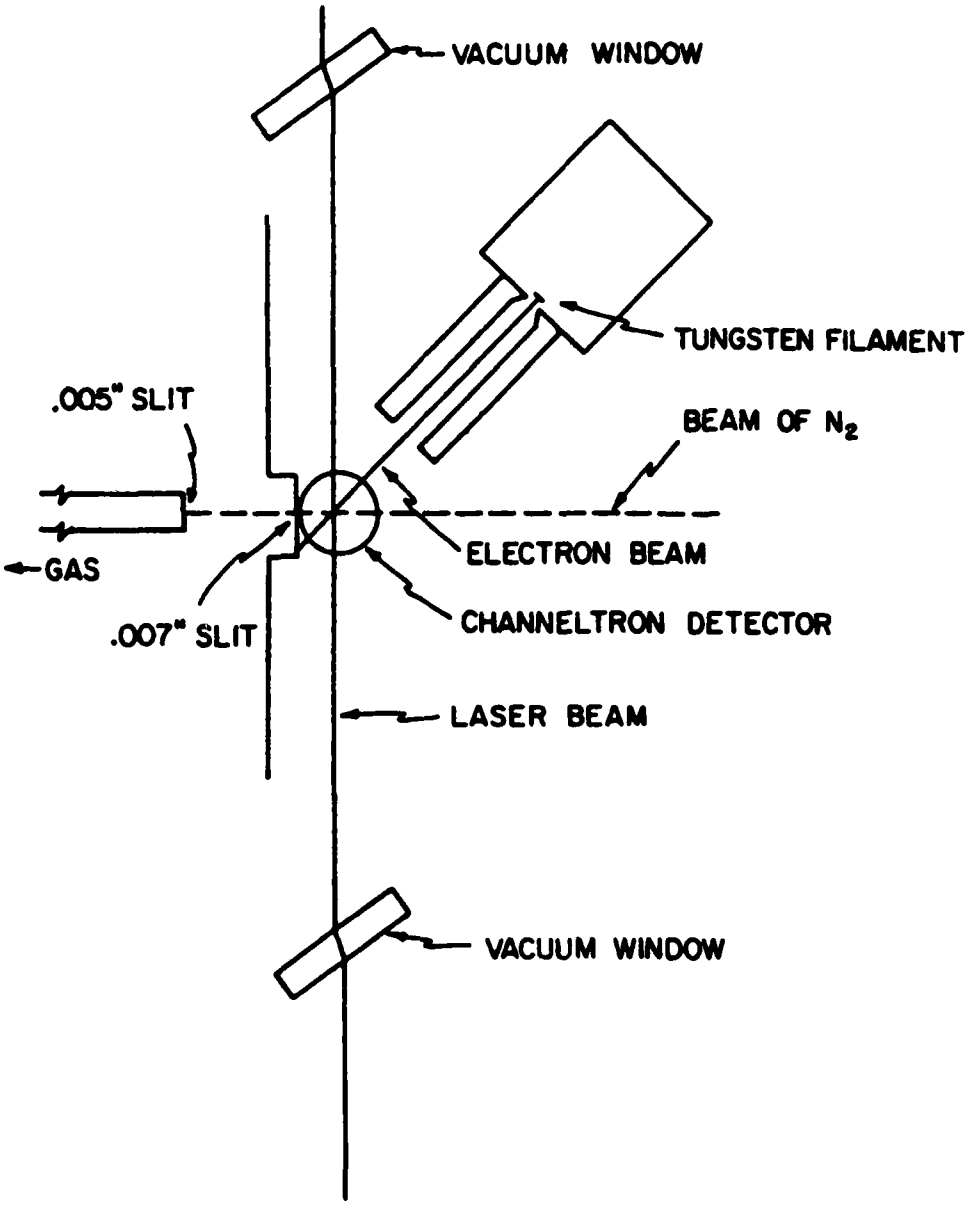
VACUUM WINDOW
TUNGSTEN FILAMENT
.005" SLIT
BEAM OF N_2
GAS
ELECTRON BEAM
.007" SLIT
CHANNELTRON DETECTOR
LASER BEAM
VACUUM WINDOW

Figure 8

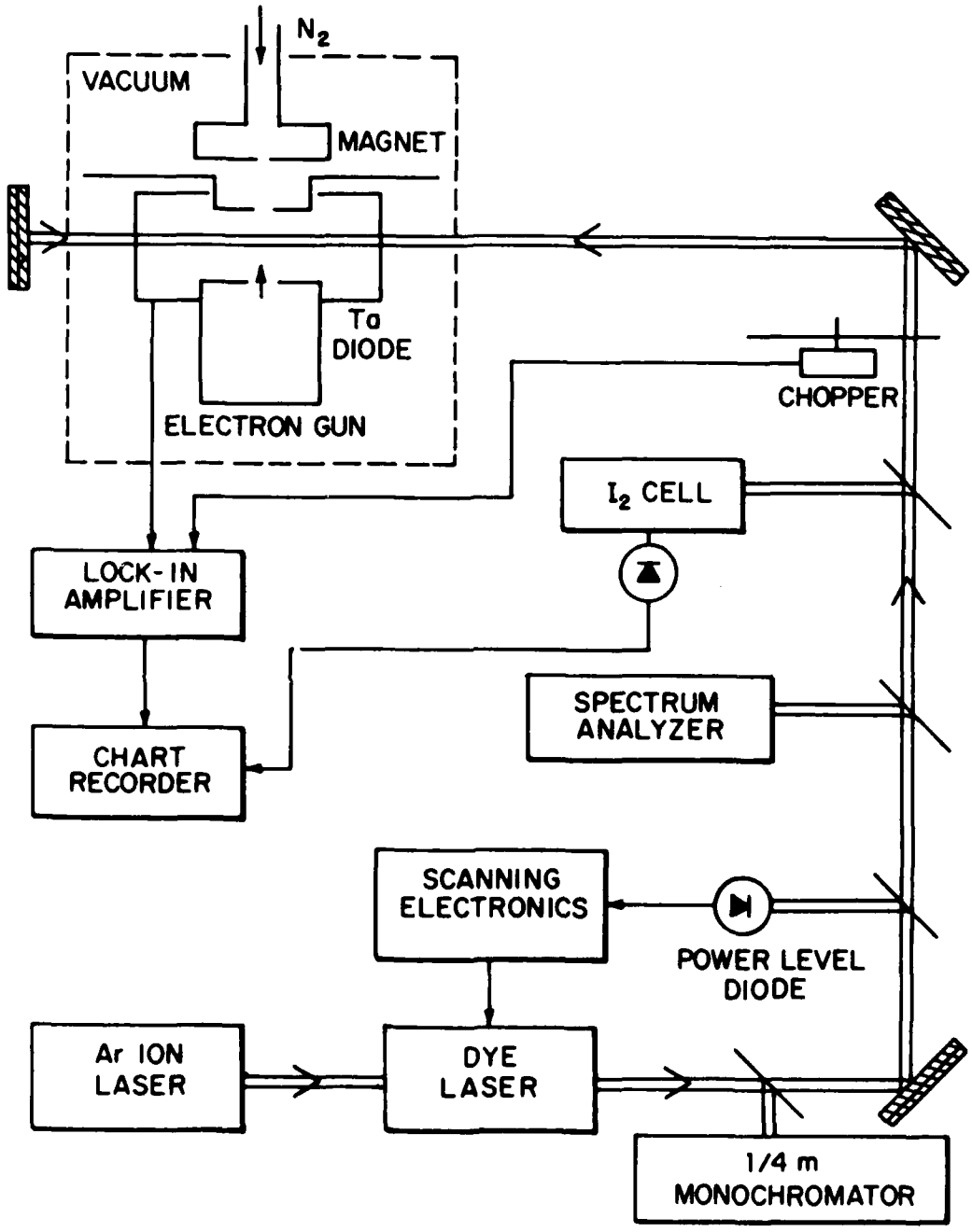
N_2
VACUUM
MAGNET
Ta
DIODE
ELECTRON GUN
CHOPPER
I_2 CELL
LOCK-IN
AMPLIFIER
SPECTRUM
ANALYZER
CHART
RECORDER
SCANNING
ELECTRONICS
POWER LEVEL
DIODE
Ar ION
LASER
DYE
LASER
1/4 m
MONOCHROMATOR

Figure 9

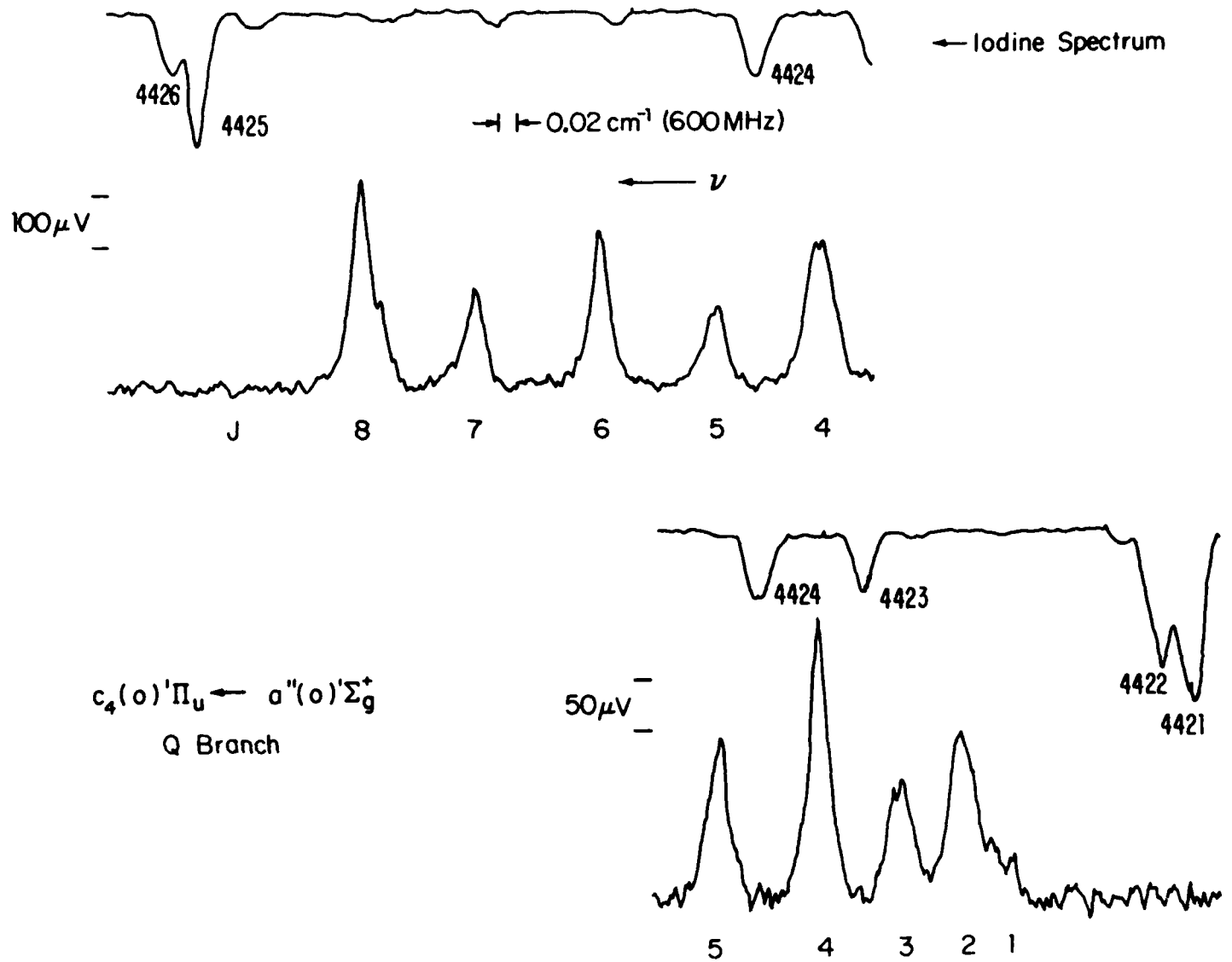
4426
4425
4424
Iodine Spectrum
0.02 cm⁻¹ (600 MHz)
ν
100μV
J
8
7
6
5
4
4424
4423
4422
4421
50μV
c₄(o)'Π_u ← a''(o)'Σ_g⁺
Q Branch
5
4
3
2
1

Figure 10

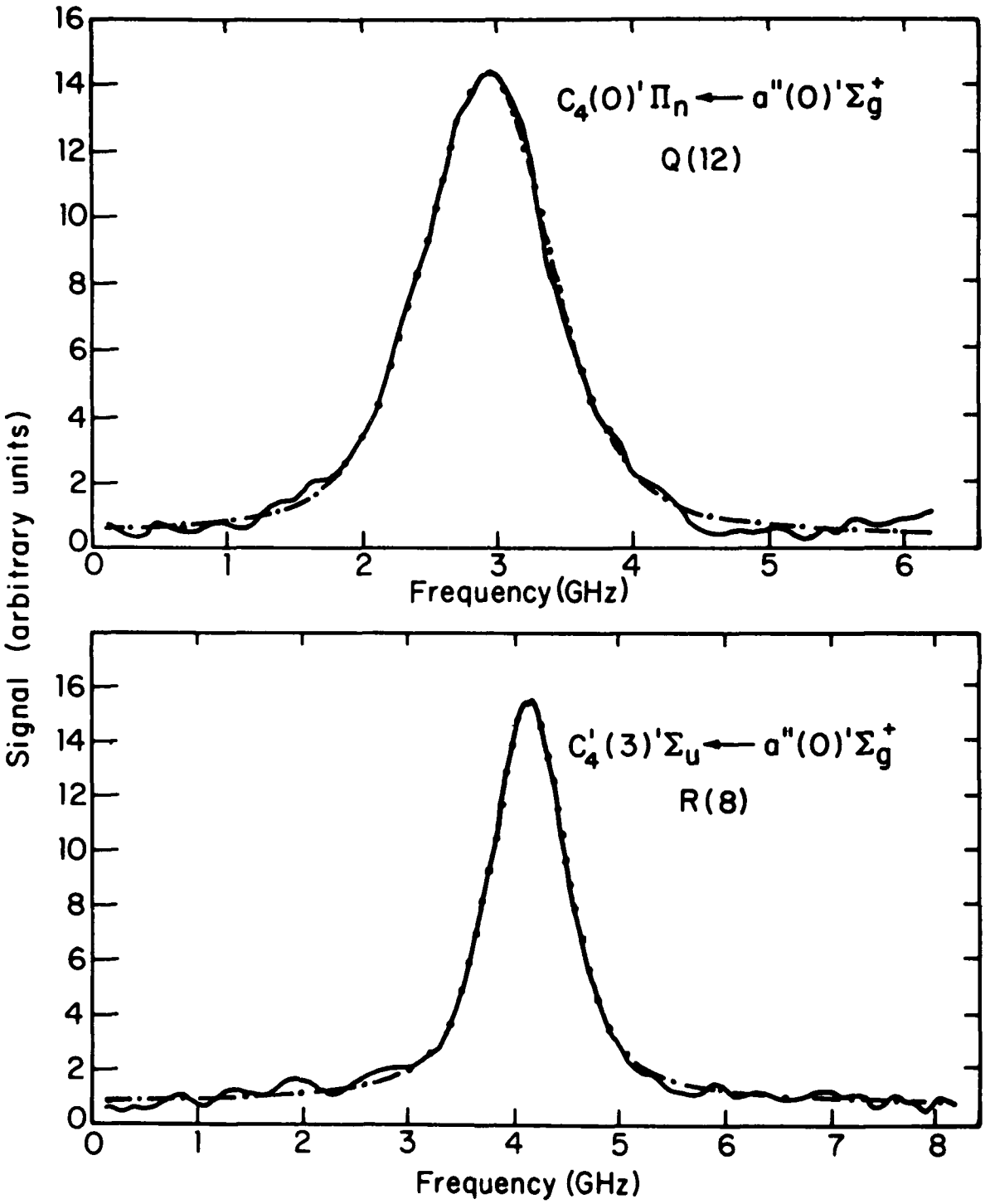
Signal (arbitrary units)
$C_4(0)'\Pi_n \leftarrow a''(0)'\Sigma_g^+$
Q(12)
Frequency (GHz)
$C_4'(3)'\Sigma_u \leftarrow a''(0)'\Sigma_g^+$
R(8)
Frequency (GHz)

Figure 11

6.0 Personnel

During the course of this project, the following individuals participated:

F. M. Pipkin	Principal Investigator
R. C. Short	Research Associate
P. Zhao	Research Associate
J. Schussler	Graduate Student
A. W. Kam	Graduate Student
M. D. Lindsay	Graduate Student

7.0 Publications

1. Paper presented at May 1987 meeting of the Division of Atomic, Molecular and Optical Physics of the American Physical Society:

Molecular Beam Study of Singlet Rydberg States of N_2, A. W. Kam, M. D. Lindsay, F. M. Pipkin, R. C. Short and P. Zhao, Bull. Am. Phys. Soc. 32, 1221 (1987).

2. Paper submitted to Physical Review Letters, October 1987:

Laser Excitation of High Rydberg States in Molecular Nitrogen, A. W. Kam, M. D. Lindsay, F. M. Pipkin, R. C. Short and P. Zhao.

8.0 Appendix

A copy of the paper reporting the observation of the singlet Rydberg states of N_2 using laser excitation out of the $a''(0)^1\Sigma_g^+$ metastable state.

Laser Observation of High Rydberg States in Molecular Nitrogen

A. W. Kam, M. D. Lindsay, F. M. Pipkin, R. C. Short* and Ping Zhao

Lyman Laboratory of Physics
Harvard University
Cambridge, Massachusetts 02138

Abstract

A combination of electron and laser excitation of nitrogen molecules in a molecular beam has been used to observe the $c_4(0)^1\Pi_u$, $c_5'(0)^1\Sigma_u^+$, and $c_4'(3)^1\Sigma_u^+$ Rydberg states. The measured linewidths are used to determine the lifetimes for the $c_4(0)^1\Pi_u$ and $c_4'(3)^1\Sigma_u^+$ states. The lifetimes are, respectively (0.46 ± 0.10) nsec and (0.25 ± 0.05) nsec.

PACS Numbers: 33.20.Ni, 33.70.Fd, 33.80.Gj

The detailed photodynamics of the nitrogen molecule is an essential component for modeling the earth's atmosphere. The excited singlet states of the N_2 molecule are sources of hard uv radiation and through predissociation excited nitrogen atoms. Despite their importance for understanding the behavior of excited N_2 molecules, relatively little is known about the decay channels for the high lying singlet states.[1,2] In this letter we report a new technique for studying the high lying singlet states of N_2 in which the output of a stabilized, tunable dye laser excites molecules in the $a''(0)^1\Sigma_g^+$ metastable state into the Rydberg states, and the transitions are observed through the change in the uv light emitted.

The term values for the states which can be reached by optical excitation from the ground state have been studied extensively by Carroll, Yoshino and their collaborators.[3-8] Several groups[9,10] used electron energy loss spectroscopy to measure the cross sections for excitation of the Rydberg states. Zipf and McLaughlin[11] used measurements of the cross sections for production of light by electrons in conjunction with the results from energy loss spectroscopy to estimate the relative branching ratios for radiative decay and predissociation. Studies of these states are made difficult by the complexity of the spectra and the large cross section for reabsorption of the emitted radiation. Recently, Roncin, et al.[12] employed a magnetically confined low pressure discharge to study with high resolution the uv light emitted in the range 80 to 110 nm. They observed in emission many bands not reported by earlier workers.

Figure 1 shows a partial energy level diagram for the singlet states of N_2. Each level corresponds to the ground vibrational state of a particular electronic configuration. Figure 2 shows a diagram of the apparatus used to excite the N_2 molecules and to observe the transitions. A 30-35 eV, 4-5 mA magnetically collimated electron beam excites the N_2 molecules in a

thermal beam. The collimation ratio of the beam is 10 to 1; the source pressure, 5 torr; the magnetic field in the interaction region, roughly 400G. The molecular beam and the electron beam are collinear and counterpropagate to maximize the region of overlap. A photodiode with a tantalum photocathode electrically shielded from stray electrons monitors the uv light emitted perpendicular to the electron beam by the excited N_2 molecules. The diode is estimated to have an average quantum efficiency of approximately 10% over the region from 40 to 110 nm.[13] The electron beam excites the molecules to the $a''(0)^1\Sigma_g^+$ metastable state and to a myriad of other short and long lived states, many of which decay with emission of uv light in the range from 40 to 110 nm. A laser beam perpendicular to the electron beam and to the central axis of the photodetector excites the molecules in the metastable $a''(0)^1\Sigma_g^+$ state to higher Rydberg states. Rhodamine 6G is used to drive transitions near 600 nm; Styrl 9M, transitions near 820 nm. A light chopper modulates the laser beam, and a lock-in detector measures the modulated component of the photocurrent. The absorption signals from an iodine cell are used to measure the wavelength of the laser.[14]

With this arrangement we were able to observe the excitation out of the $a''(0)^1\Sigma_g^+$ state even if its lifetime is very short. In earlier experiments in which the electron excitation region and the laser excitation region were separated by 1 cm or more, we were not able to detect excitation of the N_2 molecules out of the $a''(0)^1\Sigma_g^+$ state. This indicates that the lifetime of the $a''(0)^1\Sigma_g^+$ state is less than 20μsec.

Figure 3 shows the signals observed for the Q branch transition $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ together with the absorption signal from the iodine cell. The N_2 signals are due to an increase in the uv light detected; the change in the light intensity is roughly 6 parts in 10^5. A similar experiment carried out to test the [illegible] with the nitrogen replaced by neon gave signals with an increase

in the uv light detected with ow source pressures (0.4 torr) and a decrease with high source pressures. As the pressure increased the signal in the wings of the line changed sign first and then the signal at the center decreased and changed sign. This behavior was quite surprising. The $1s_5(^3P_2)$ metastable level in neon, which corresponds to the $a''(0)^1\Sigma_g^+$ state, does not decay with emission of uv radiation; the $1s_2(^1P_1)$ and $1s_4(^3P_1)$ levels, which are populated through radiative decay after laser excitation to the $2p_2(^3P_1)$ level, decay rapidly with the emission of uv radiation. Thus one would expect to see an increase in the uv light emitted. The change in the sign of the signal is attributed to a combination of reabsorption of the emitted uv radiation and laser depopulation of the metastable atoms which play a role in the electron excitation to higher levels which emit uv radiation. The nitrogen is less susceptible to this reversal since the emitted uv light comes in large part from transitions to high vibrational levels of the ground state which are not populated at room temperature and the $a''(0)^1\Sigma_g^+$ state has a shorter lifetime than the metastable states in neon.

The only observation of uv light emitted by the $a''(0)^1\Sigma_g^+$ state is that reported by Lutz.[15] Dressler and Lutz[16] used the absorption in nitrogen gas at several pressures to observe the absorption band for the transition $a''(0)^1\Sigma_g^+ \leftarrow X(0)^1\Sigma_g^+$. Lutz[15] subsequently reported the observation of the $a''(0)^1\Sigma_g^+ \rightarrow X(0)^1\Sigma_g^+$ transition in emission from a discharge at 101.005 nm. The near lying intense bands from other transitions made the observation of this transition difficult. Lutz's observation has not been confirmed by later workers. The term value 99005.0 cm^{-1} calculated from the wavelength measured by Lutz differs by 165 cm^{-1} from the term value 98840.55 cm^{-1} derived in a more recent analysis by Yoshino and Freeman.[8]

This same technique has been used to observe transitions from the $a''(0)^1\Sigma_g^+$ state to the $c_5'(0)^1\Sigma_u^+$ and the $c_4'(3)^1\Sigma_u^+$ states. In each case the signals were due to an increase in the uv light detected.

The change in the uv light emitted was roughly the same for all three transitions. If the change in the last light emitted is due simply to the emission by the laser excited $c_4(0)^1\Pi_u$, $c_5'(0)^1\Sigma_u$ and $c_5'(3)^1\Sigma_u^+$ states, then this does not support the conclusion of Zipf and McLaughlin[11] concerning predissociation in the excited singlet states of N_2. Zipf and McLaughlin concluded that the $c_4'(3)^1\Sigma_u^+$ state decayed through predissociation 15% of the time and the $c_4(0)^1\Sigma_u$ and $c_5'(0)^1\Sigma_u^+$ states decayed through predissociation more than 99% of the time. Roncin, et al.[12] reported that the uv radiation from the $c_4'(3)^1\Sigma_u^+$ state is very strong, the uv radiation from the $c_4(0)^1\Pi_u$ state is weak, and the uv radiation from the $c_5'(0)^1\Sigma_u$ state is very weak. There are clearly discrepancies between these observations which merit further investigation.

Figure 4 shows the observed line profile for the R(8), $c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transition. A fit to a Voigt profile gave (640 ± 130) MHz for the Lorentzian component and (530 ± 100) MHz for the Gaussian component. The width of the Lorentzian component corresponds to a lifetime of (0.25 ± 0.05) nsec. Similar observations for the Q(12), $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ transition gave a lifetime of (0.46±0.10) nsec. These lifetimes are similar to the reported lifetimes for other $^1\Pi_u$ and $^1\Sigma_u^+$ states.[17-19]

Table 1 summarizes the measured line position for each of the transitions observed. Also shown are the line positions determined by Suzuki and Kakimoto[20] for the same transitions through optogalvanic spectroscopy or calculated from the uv absorption measurements of Yoshino, Freeman and Tanaka.[7] In all cases the agreement is satisfactory.

This combination of electron beam and laser excitation provides a new tool for the study of the high lying Rydberg states of N_2. Two lasers can be used to extend the studies to the s and d Rydberg levels which are not accessible by optical absorption from the ground state. The replacement of the photodiode detector with a uv spectrometer will allow one to observe in detail the spectral redistribution of the radiation. This should make it feasible to observe transitions to other Rydberg states, to observe transitions to the $b^1\Pi_u$ and $b'^1\Sigma_u^+$ valence states, to study the levels in greater detail, to measure the relative branching ratios for radiative decay and predissociation, to measure for each state the branching ratios for decay to the different vibrational levels of the ground state, and to measure the branching ratios for decay to the $a^1\Pi_g$ metastable state.

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Table 1

A summary of the observed transition intervals in cm^{-1}. The other measurements for the $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ and $c_5'(0)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transitions are those of Suzuki and Kakimoto.[20] They estimate the reproducibility of their measurements is roughly 0.001 cm^{-1}. The intervals for the $c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transitions were calculated from the term values determined by Yoshino, et al.[7]

Transition	Other Work	This Work	Difference
	$c_4'(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$		
Q(1)	16725.154	16725.150±0.010	-0.004
Q(2)	16725.202	16725.197±0.004	-0.005
Q(3)	16725.271	16725.266±0.003	-0.005
Q(4)	16725.362	16725.359±0.003	-0.003
Q(5)	16725.476	16725.470±0.003	-0.006
Q(6)	16725.608	16725.599±0.005	-0.009
Q(7)	16725.765	16725.758±0.011	-0.007
Q(8)	16725.883	16725.888±0.019	+0.005
Q(12)	16727.037	16727.022±0.010	-0.015
R(1)	16732.768	16732.759±0.010	-0.009
R(6)	16751.416	16751.398±0.010	-0.018
R(14)	16776.607	16776.592±0.010	-0.015
	$c_5'(0)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$		
P(14)	16845.886	16845.877±0.010	-0.009
	$c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$		
R(6)	11825.133±0.300	11825.172±0.010	0.039
R(7)	11823.494±0.300	11823.695±0.010	0.201
R(8)	11821.308±0.300	11821.399±0.005	0.091

References

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1. For a comprehensive review of the data on the nitrogen molecule available prior to 1977, see A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
2. For a recent discussion of the role of these states in auroral emission, see T. G. Slanger, Planet. Space Sci. 31, 1525 (1983).
3. P. K. Carroll, C. P. Collins, and K. Yoshino, J. Phys. B3, L127 (1970).
4. P. K. Carroll and K. Yoshino, J. Phys. B5, 1614 (1972)
5. K. Yoshino, Y. Tanaka, P. K. Carroll, and P. Mitchell, J. Mol. Spectrosc. 54, 87 (1975).
6. K. Yoshino and Y. Tanaka, J. Mol. Spectrosc. 66, 219 (1977).
7. K. Yoshino, D. E. Freeman, and Y. Tanaka, J. Mol. Spectrosc. 76, 153 (1979).
8. K. Yoshino and D. E. Freeman, Can. J. Phys. 62, 1478 (1984).
9. J. Geiger and B. Schroeder, J. Chem. Phys. 50, 7 (1969).
10. E. N. Lassettre, in Methods of Experimental Physics, Ed. by D. Williams (Academic Press, New York, 1974) Vol. 3, Part B, p. 868.
11. E. C. Zipf and R. W. McLaughlin, Planet. Space Sci. 26, 449 (1978).
12. J.-Y. Roncin, F. Launay, and K. Yoshino, Planet Space Sci. 35, 267 (1987).
13. J. A. R. Samson, in Techniques of Vacuum Ultraviolet Spectroscopy (John Wiley and Sons, New York, 1967), p. 229.
14. S. Gerstenkorn and p. Luc, Atlas du Spectre D'Absorption de la Molecule D'Iode (CRNS, Paris, 1978). A systematic correction is described by S. Gerstenkorn and P. Luc, Rev. Phys. Appl. 14, 791 (1979).
15. B. L. Lutz, J. Chem. Phys. 51, 706 (1969).

16. K. Dressler and B. L. Lutz, Phys. Rev. Lett. 19, 1219 (1967).

17. J. E. Hesser and K. Dressler, J. Chem. Phys. 45, 3149 (1966).

18. J. E. Hesser, J. Chem. Phys. 48, 2518 (1968).

19. H. Oertel, M. Kratzat, J. Imschweiler, and T. Noll, Chem. Phys. Lett. 82, 552 (1981).

20. T. Suzuki and M. Kakimoto, J. Mol. Spectrosc. 93, 423 (1982).

Figure Captions

Fig. 1 -- An energy level diagram showing the singlet Rydberg states of interest in this experiment. Only the ground vibrational level for each electronic state is shown.

Fig. 2 -- A schematic diagram of the apparatus used to excite the N_2 molecules and observe the transitions.

Fig. 3 -- The Q band $c_4(0)^1\Pi_u \leftarrow a''(0)^1\Sigma_g^+$ transitions near the band head. The numbers on the iodine lines are the identification numbers in the iodine atlas.

Fig. 4 -- The observed line profile for the R(8), $c_4'(3)^1\Sigma_u^+ \leftarrow a''(0)^1\Sigma_g^+$ transition. The dot-dash curve is the fit using a Voigt line profile.

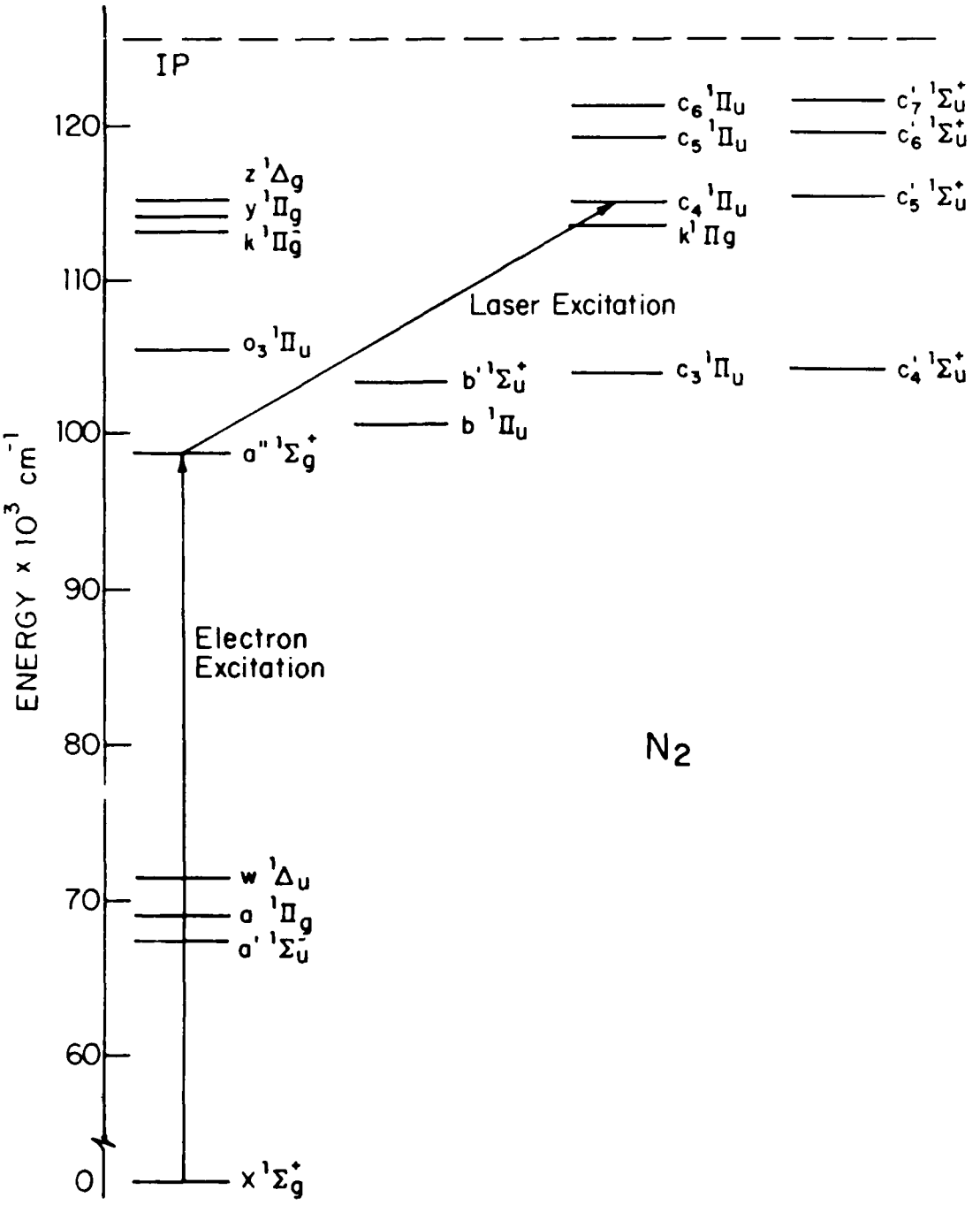
IP
120
110
100
90
80
70
60
0
ENERGY x 10^3 cm^{-1}
$z\,^1\Delta_g$
$y\,^1\Pi_g$
$k\,^1\Pi_g$
$o_3\,^1\Pi_u$
$a''\,^1\Sigma_g^+$
$w\,^1\Delta_u$
$a\,^1\Pi_g$
$a'\,^1\Sigma_u^-$
$x\,^1\Sigma_g^+$
$b'\,^1\Sigma_u^+$
$b\,^1\Pi_u$
$c_6\,^1\Pi_u$
$c_5\,^1\Pi_u$
$c_4\,^1\Pi_u$
$k'\,^1\Pi_g$
$c_3\,^1\Pi_u$
$c_7'\,^1\Sigma_u^+$
$c_6'\,^1\Sigma_u^+$
$c_5'\,^1\Sigma_u^+$
$c_4'\,^1\Sigma_u^+$
Laser Excitation
Electron Excitation
N_2

Figure 1

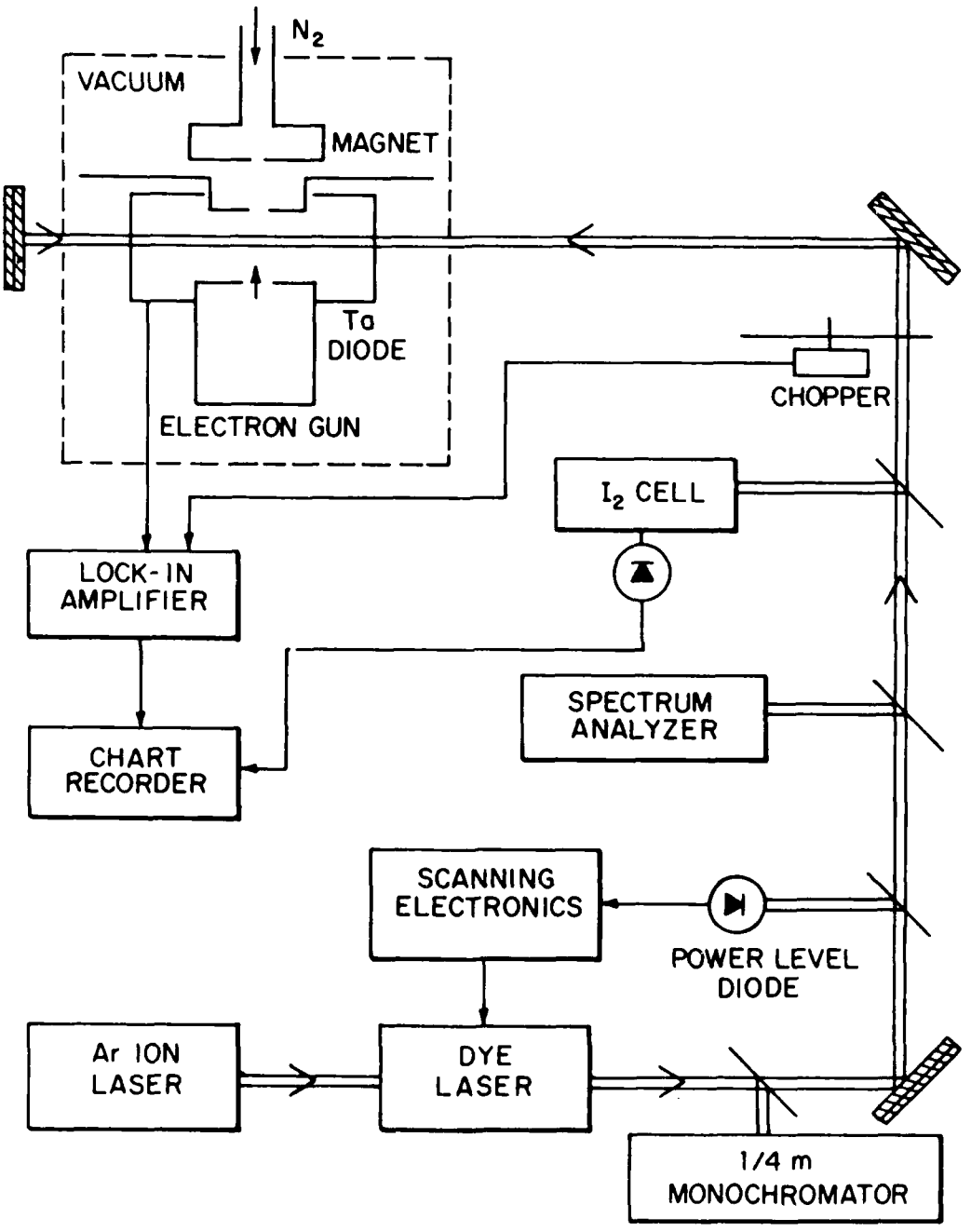
N_2
VACUUM
MAGNET
To DIODE
ELECTRON GUN
CHOPPER
I_2 CELL
LOCK-IN AMPLIFIER
SPECTRUM ANALYZER
CHART RECORDER
SCANNING ELECTRONICS
POWER LEVEL DIODE
Ar ION LASER
DYE LASER
1/4 m MONOCHROMATOR

Figure 2

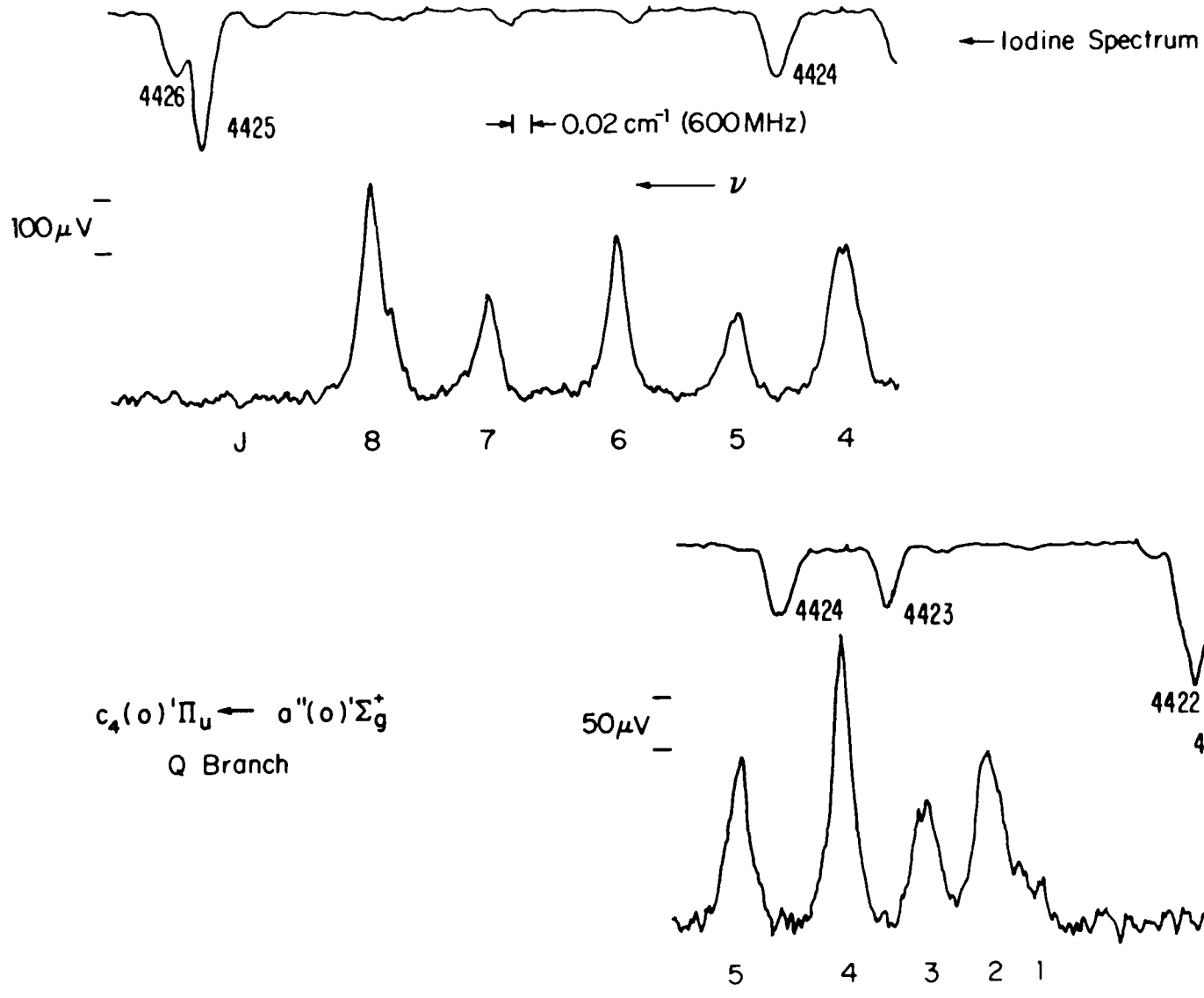
4426
4425
4424
Iodine Spectrum
0.02 cm⁻¹ (600 MHz)
ν
100 μV
J
8
7
6
5
4
4424
4423
4422
4421
50 μV
c₄(o)¹Π_u ← a''(o)¹Σ_g⁺
Q Branch
5
4
3
2
1

Figure 3

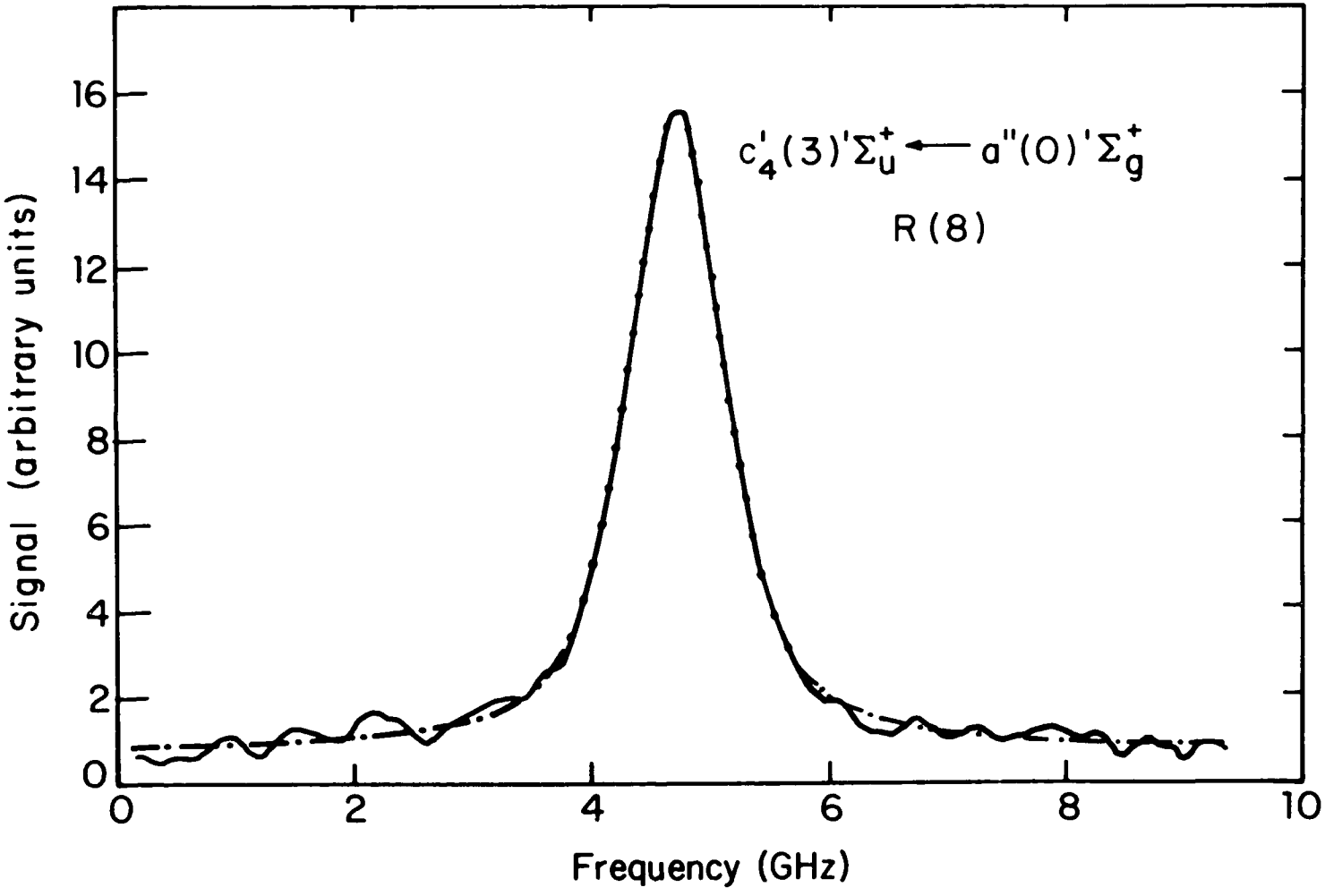
Signal (arbitrary units)
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
Frequency (GHz)
$c_4'(3)'\Sigma_u^+ \leftarrow a''(0)'\Sigma_g^+$
R(8)

Figure 4

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